

ND ENERGY STUDENT RESEARCH FELLOWSHIP FINAL REPORT

STUDENT NAME:	Amal Sebastian
FACULTY ADVISOR:	Prof. Sylwia Ptasinska, Ph. D
REPORT PERIOD:	03/1/19 – 12/1/19
PROJECT TITLE:	Atmospheric pressure plasma: An alternative tool for the synthesis of efficient photocatalytic materials.
CONNECTION TO ND ENERGY'S RESEARCH AREAS (CHECK ALL THAT APPLY):	<input checked="" type="checkbox"/> Energy Conversion and Efficiency <input type="checkbox"/> Sustainable and Secure Nuclear <input type="checkbox"/> Smart Storage and Distribution <input checked="" type="checkbox"/> Transformation Solar <input type="checkbox"/> Sustainable Bio/Fossil Fuels <input type="checkbox"/> Transformative Wind

MAJOR GOALS AND ACCOMPLISHMENTS:

List your major research goals and provide a brief description of your accomplishments (1-2 sentences). Indicate the percentage completed for each goal. Please use a separate sheet to share additional details, technical results, charts, and graphics.

MAJOR RESEARCH GOALS	ACTUAL PERFORMANCE AND ACCOMPLISHMENTS	% OF GOAL COMPLETED
Design a proper experimental set-up to deposit the desired films (TaON) with atmospheric pressure plasma (APP) jet.	Was able to get the desired deposition using a classic dielectric barrier discharge atmospheric pressure plasma with a proper jet environment.	100 %
Tune and vary the numerous APP parameters to see the surface chemistry changes using XPS.	Was able to modify TaON / Ta oxides ratio by tuning APP parameters. (N ₂ flow rate, deposition time) Need to tune other APP parameters such as Voltage and pulsing frequency.	50 %
Find the optimal deposition conditions by a predictive modeling approach using all known APP parameters. (Voltage, Pulsing Frequency, Deposition time, Flow rate of feed gas (N₂), Flow rate of primary gas (He)	Need huge data sets to do predictive modelling and we are currently doing data acquisition to achieve that. We will employ machine learning tools to find the optimal deposition conditions. Choosing 4 combinations for each of these tunable APP parameters (Voltage, pulsing frequency, Deposition time, , Flow rate of feed gas (N ₂), Flow rate of primary gas (He)) would yield almost 1024 combinations of data which is experimentally more challenging to achieve.	20 %

RESEARCH OUTPUT:

Please provide detailed information below regarding any output resulting from your research project.

CATEGORY	INFORMATION
EXTERNAL PROPOSALS	(Sponsor, Project Title, PIs, Submission Date, Proposal Amount)
EXTERNAL AWARDS	(Sponsor, Project Title, PIs, Award Date, Award Amount)
JOURNAL ARTICLES	(Journal Name, Title, Authors, Submission Date, Publication Date, Volume #, Page #s)
BOOKS AND CHAPTERS	(Book Title, Chapter Title, Authors, Submission Date, Publication Date, Volume #, Page #s)

PUBLIC PRESENTATIONS, SEMINARS, LECTURES	(Event, Presentation Title, Presentation Date, Location)
1) POSTER	American Vacuum Society (AVS) Conference 66, Atmospheric pressure plasma: An alternative tool for the synthesis of efficient photocatalytic materials, 10/22/19 , Greater Columbus convention center, Columbus OH
2) POSTER	ND research sustainability expo 2019, Atmospheric pressure plasma: An alternative tool for the synthesis of efficient photocatalytic materials, 09/16/19, University of Notre Dame
3) POSTER	COSE – JAM for Graduate students 2019, Atmospheric pressure plasma: An alternative tool for the synthesis of efficient photocatalytic materials, 12/13/19 , University of Notre Dame
AWARDS, PRIZES, RECOGNITIONS	(Purpose, Title, Date Received)
INTERNAL COLLABORATIONS FOSTERED	(Collaborator Name, Organization, Purpose of Affiliation)
EXTERNAL COLLABORATIONS FOSTERED	(Collaborator Name, Organization, Purpose of Affiliation)
WEBSITE(S) FEATURING RESEARCH PROJECT	(URL)
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	(Please describe each item in detail)

MAJOR GOALS AND ACCOMPLISHMENTS
(Additional Details, Technical Results, Charts and Graphics)

Atmospheric pressure plasma: An alternative tool for the syn- thesis of efficient photocatalytic materials

Amal Sebastian and Sylwia Ptasinska

Radiation Research Laboratory and Department of Physics, University of Notre Dame

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Photocatalytic splitting of water into hydrogen and oxygen is a method to convert solar energy into storable chemical energy directly, and it has received significant attention for its high potential for low cost and clean energy production. Developing efficient and cost-effective photocatalysts for water splitting is a growing need for solar energy research. In this work, we propose an alternative method to deposit photocatalytic materials with atmospheric pressure plasma (APP). The design and experimental approach for depositing the narrow bandgap photocatalyst Tantalum oxynitride (TaON) using APP, with a suitable solution precursor are explained in detail. The effect of plasma parameters on the composition of films is investigated by monitoring the surface chemistry changes with X-ray photoelectron spectroscopy. The observed changes in the composition of films with modulation of plasma parameters hint towards alternative processing routes to deposit photocatalytic materials efficiently.

1 Introduction

Photocatalytic water splitting is emerging as a promising technique to store solar energy in the form of energy-dense hydrogen fuel. One of the prominent challenges in solar energy research is to develop efficient and cost-effective photocatalysts for water splitting.

Though there are numerous traditional methods to prepare photocatalytic materials, most of them relies on vacuum-based techniques. These are often costly and complex. Atmospheric pressure plasma (APP) discharges, being a novel and versatile technique, is one of the emerging tools to cost-effective solutions for many processing challenges in material science. Its feasibilities in modifying surfaces, and depositing materials with minimal chemical waste have always fascinated the scientific community.

Though depositions of highly efficient photocatalytic materials was able to achieve with atmospheric pressure plasmas previously, most of them were titanium dioxide based^{1–5}. But the very high bandgap of TiO₂ (3.2 eV) limits its use as photoelectrodes, and is often employed in photoelectrochemical solar cells as a protective coating rather than as a proper photoelectrode material. This drives us to think of alternative photocatalytic materials if any that can potentially be deposited with atmospheric pressure plasma.

*Atmospheric pressure plasma:
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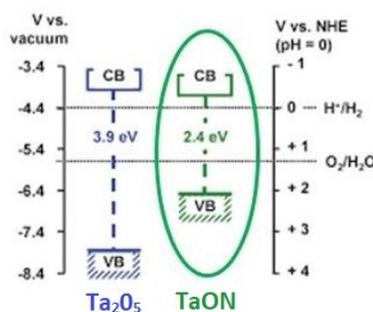


Figure 1: Oxide and oxynitride based photocatalysts of Ta. TaON has a narrow bandgap of 2.1-2.4 eV. Figure adapted from Reference 12

In order to disentangle this, we have to have an understanding of the various chemical species that are present in atmospheric pressure plasma. Plasma in general, particularly those at atmospheric pressure, is a reservoir for a lot of reactive radicals and ions that can chemically interact with a target. Highly reactive oxygen and nitrogen species (RONS) is one among those entities, and its impact on various applications of plasma is enormous. RONS created by APP in an air environment make APP an ideal tool for depositing oxynitride based materials. This benefit about APP has been successfully used and exploited by the scientific community to deposit the oxynitride films of Silicon^{6,7}, Aluminum^{8,9}, and certain metals¹⁰, in a very efficient way. Photocatalytic capabilities of oxynitride materials, particularly that of metal oxynitrides^{12,13} has been a subject of interest for a few years as well.

And hence, metal oxynitrides can undoubtedly serve as an excellent candidate to be considered for alternative photocatalyst synthesis with APP. In this work, we propose a method to deposit metal oxynitride photocatalytic materials with APP. Tantalum oxynitride (TaON) is one of the most promising metal oxynitrides for photoelectrode applications^{14,15}. It's photostability, narrow bandgap (2.2 eV), and suitable band edge positions as photoanodes have attracted much recent research attention. The primary objective of this project is to frame a proper design to deposit tantalum oxynitrides using APP which will be followed by finding the optimum deposition conditions for film. The outcome of this project can possibly open a new route to think of alternative deposition tools like APP which can offer economy and effectiveness at the same time.

2 Why plasma?

Simplicity and economy are one among the supreme qualities that makes plasma based deposition processes a very strong candidate. Plasma has proven to be cost-effective when compared to other deposition techniques such as molecular beam epitaxy, RF sputtering, sol-gel synthesis etc^{1,3}.

Compared to the compact deposition methods under vacuum conditions, atmospheric plasma-based deposition is a more robust technology which enables the deposition of coatings on substrates of various sizes regardless of their geometry^{1,4}. The latter feature of APP stems from the fact that the size of the substrate that can be treated in vacuum based deposition method is limited by the size of the chamber and that make APP a unique tool to achieve the deposition on the substrate of any size and shape.

Plasma enhanced deposition techniques also offer the benefit of minimal chemical waste throughout the process and are solvent-free when compared to other methods such as sol-gel process^{1,5}, chemical vapor deposition etc. Deposition of photocatalytic coatings with plasma assisted methods in general can also provide significant rates of deposition ($\mu\text{m}/\text{min}$)^{4,5} than the traditional methods such as chemical vapor deposition, sol-gel process, RF sputtering etc.

In addition to these benefits, The ability of APP to tune porosity and crystallinity along with its aptness in chemically modifying deposited films makes it an attractive candidate to prepare photocatalytic materials as well. The scope of this project is to effectively use such properties of APP to deposit suitable photocatalytic materials successfully. This project hence would shed light on this vital problem and will allow us to explore how effectively we can deposit photocatalytic materials using plasma.

3 Experimental design and method

The deposition method involves the use of a suitable liquid precursor spread over a suitable substrate, followed by the plasma treatment. The plasma used for treatment is a classic dielectric barrier discharge plasma at atmospheric pressure or atmospheric pressure plasma jet.

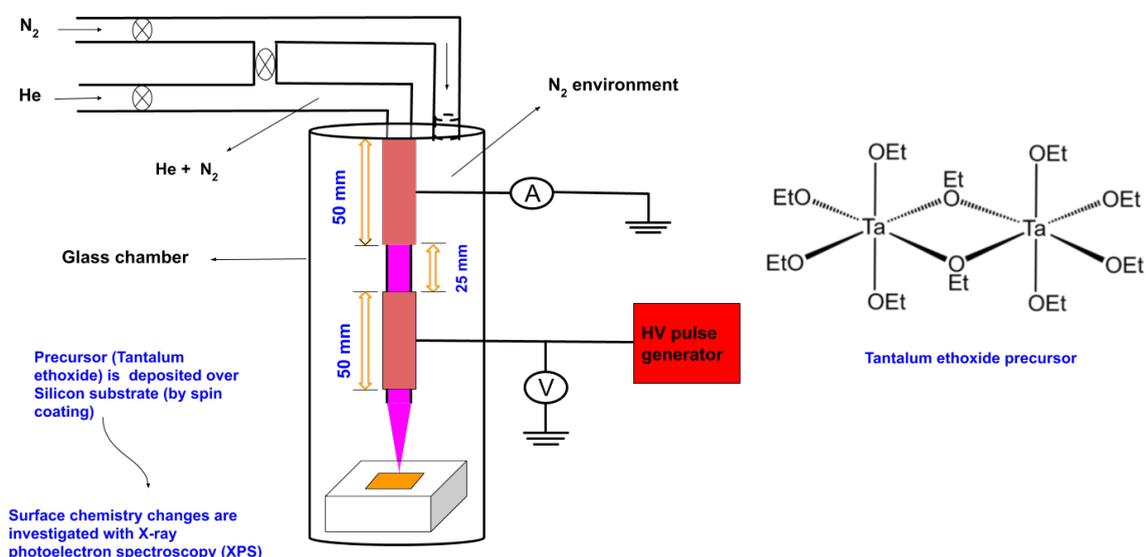


Figure 2: TaO_xN_y deposition design. Tantalum ethoxide precursor is spin-coated on Si substrate followed by plasma treatment in a proper jet environment. Tunable plasma parameters: voltage, frequency for pulsing voltage, N_2 flow rate, deposition time and He flow rate.

Plasma source: The APPJ source^{6,16} consisted of two brass electrodes, grounded and powered electrodes, separated by 25 mm and are located on the outside of a fused silica capillary, as shown in Figure 2. The fused silica capillary has an orifice diameter of 10 mm and serves as a dielectric here. If the Voltage is applied continuously, that will lead to thermalization and will transform to arcing stemming from higher discharge currents. Hence the voltage was pulsed with a square pulse generator to prevent arcing and thermalization.

The helium and N_2 flow rate through the capillary were adjusted with a flow controller. The applied voltage and plasma discharge current were measured at the powered and grounded electrodes using a high voltage probe and an induction coil current monitor, respectively. The amplitude and shape of the waveforms of voltage and current were recorded using an oscilloscope. The plasma was ignited between the two electrodes, and a visible plasma jet of a few centimeters was projected through the fused silica capillary into the open atmosphere.

Since oxidation can hugely impact the deposition procedure, it is very imperative to isolate the sample from outside atmosphere. This is achieved with the help of N_2 shielding gas environment. The flow rate for the primary He gas was kept at 5 slm (standard litre per minute), and flow for shielding gas flow rate was kept at 6 slm.

Precursor: The precursor used is Tantalum ethoxide, which is a commonly used precursor used for Tantalum oxide synthesis. The precursor was dissolved in ethanol in 1: 200 molar ratio and spin-coated on n-100 si wafer substrate using spin coater with a rotation speed of 2000 rpm and revolution time of 20s. This is followed by the treatment with plasma at various combinations of N_2 flow rate and deposition time. The interaction of precursor molecules with the excited species in plasma is believed to result in lower activation energy for the film growth, and that can promote a high-quality deposition. This interaction can be optimized and controlled by the changing plasma parameters such as plasma power, pulse frequency, feed gas volume, irradiation time, irradiation distance, etc.

The optimal deposition conditions can be obtained by tuning these various plasma parameters and subsequently monitoring the surface chemistry with X-ray photoelectron spectroscopy (XPS). In XPS, the binding energies for

the photoelectrons were calculated by measuring the kinetic energy of the emitted photoelectrons. Since each characteristic element has a unique B.E spectrum, XPS can be used as a strong surface characterization method to understand the chemistry at the surface.

X-ray photoelectron spectroscopy: The UHV XPS used has a SPECS PHOIBOS 150 hemispherical analyser⁶ equipped with a Micro-FOCUS 600 X-ray monochromator. The aluminum (Al) $K\alpha$ (1486.6 eV) X-ray source was operated at a power of 60W with an anode voltage of 12 kV and current of 5 mA. The photoelectron energy analyser was operated in fixed analyser transmission (FAT) mode. The FAT mode was selected to keep the resolution independent of the kinetic energy of the detected photoelectrons.

High-resolution spectra for the Ta 4f, N 1s, C 1s, O 1s were obtained using lower energy step of 0.05 eV. To monitor the changes happening in the substrate chemistry, Si 2p spectrum was recorded before and after the treatment as well.

In the initial phase of this project, we have kept the voltage and pulse frequency at a constant value and the potential impact of deposition time and secondary gas N_2 flow rate was studied. The Voltage, frequency was kept at 8 kV and 2000 Hz, respectively and the secondary N_2 flow rate and deposition time were varied. The N_2 flow rate was varied from 10 sccm - 30 sccm (standard cm^3 per minute) and deposition time was varied from 15 minutes to 35 minutes.

The changes in the surface chemistry by changing these parameters were monitored with XPS and the results are shown in the next section.

4 Preliminary results

Figure 3 shows the Ta 4f, N 1s and C 1s core level spectra acquisition of the films before and after the treatment. In order to understand the various bonding environments of Ta, the Ta 4f peaks were fitted with different sets of doublet peaks using Casa XPS, a XPS spectra analysis software. The doublet peak stems from the spin-orbit splitting for 4f orbital which leads to $4f_{5/2}, 4f_{7/2}$ peaks, and each doublet for the Ta 4f deconvoluted spectra corresponds to a particular bonding state.

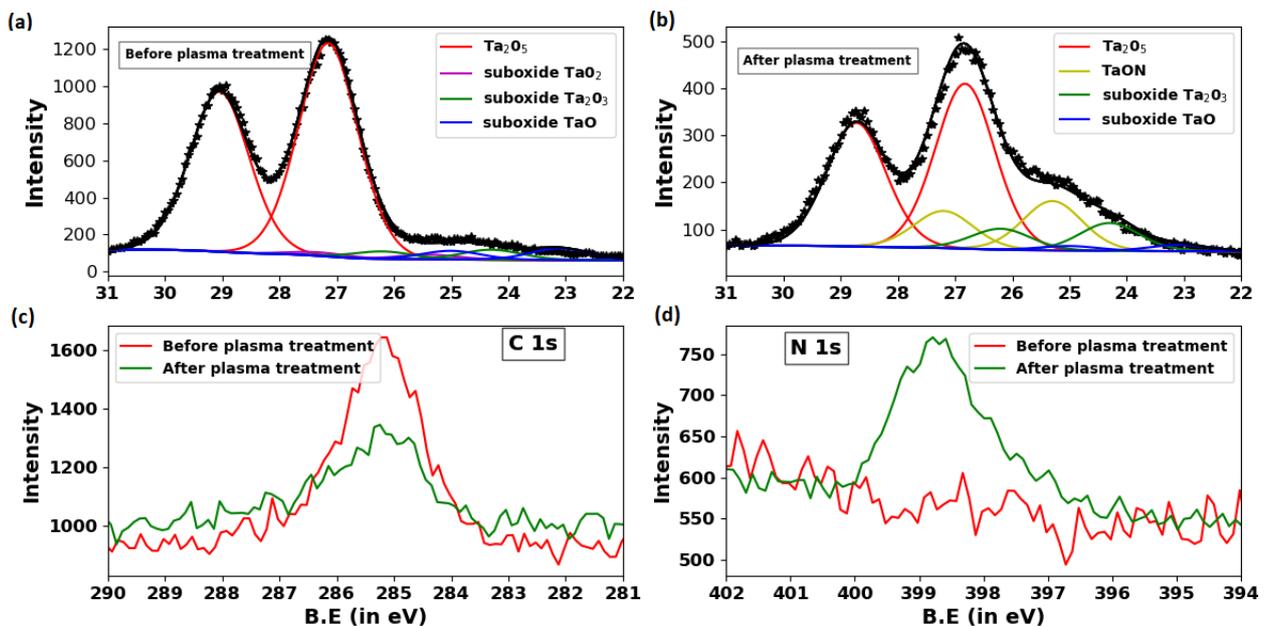


Figure 3: High-resolution Ta 4f XPS spectra acquired; (a) before the plasma treatment ; (b) After APP treatment using parameters N_2 flow= 30 SCCM, treatment time= 25 mins, V = 8 kV, Frequency= 2000 Hz. Fitted spectra after plasma treatments indicate oxynitride formation (c) C 1s spectra before and after the plasma treatment at the same set of plasma parameters as (b); (d) N 1s spectra obtained for the same set of parameters

Ta bond	Binding energy (ev)	
	Ta 4f _{7/2}	Ta 4f _{5/2}
Ta ₂ O ₅ (Ta ⁵⁺)	27.0	28.9
TaON (Ta ⁵⁺)	25.3	27.2
TaO ₂ (Ta ⁴⁺)	25.5	27.4
Ta ₂ O ₃ (Ta ³⁺)	24.3	26.2
TaO (Ta ²⁺)	23.1	25.0

Table 1: Summary of Ta 4f B.E positions used to fit the spectra.

In the pure precursor, peak intensities are mostly dominated by Ta 4f_{5/2} and Ta 4f_{7/2} appearing at 28.9 eV and 27 eV. These BE's positions correspond to the well reported doublet states of Ta₂O₅^{17–19}. The shoulder of Ta 4f at lower binding energies corresponds to doublet states of Ta suboxides, namely TaO₂ (in Ta⁴⁺ state), Ta₂O₃ (in Ta³⁺ state) and TaO (Ta²⁺). The details of the peak assignments are provided in table 1. The peak separation of each of these doublet states of Ta 4f (between 5/2 and 7/2 peaks) is 1.9 eV which is in agreement with the reported values in the references^{17–21}.

For the plasma treated films, a pronounced shoulder appears in Ta 4f peak due to doublet peaks at 27.2 and 25.3 eV. These doublet peaks correspond to the Ta⁺⁵ state of TaON bond^{20,21} and that indicate the formation of oxynitrides at the surface. The presence of oxynitrides are established with the presence of nitrogen 1s peaks as well. The quenching of carbon peaks after the plasma treatment arises due to the removal of carbon atoms from the precursor in the form of volatile carbon compounds.

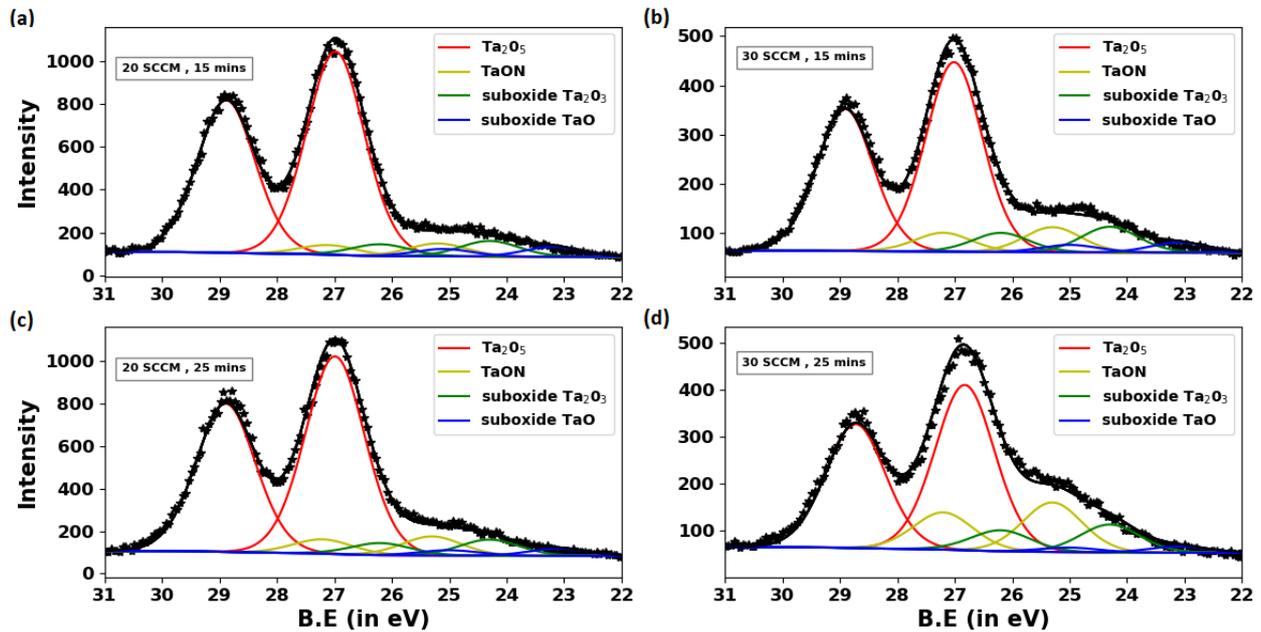


Figure 4: The effect of N₂ flow rates in the oxynitride bond formation: (a) Ta 4f spectra for a flow rate of 20 sccm at a treatment time of 15 minute;(b) Spectra obtained when the flow rate was changed to 30 sccm at the same treatment time as (a);(c) Ta 4f spectra obtained at a flow rate of 20 sccm with treatment time of 25 minutes;(d) Spectra acquired at 30 sccm flow for the same treatment time as (c).

The fraction of TaON bonds formed at the surface can be evaluated by taking the peak area ratios from the obtained fits. This ratio seems to change with the plasma parameters, and the goal is to find the optimal parameters which would maximise the TaON bond formation.

The results of changing the flow rate at treatment times of 15 minutes and 25 minutes are shown in figure 4. The oxynitride ratio enhancement with the nitrogen flow rate indicates that more nitridation happens at higher flow rates.

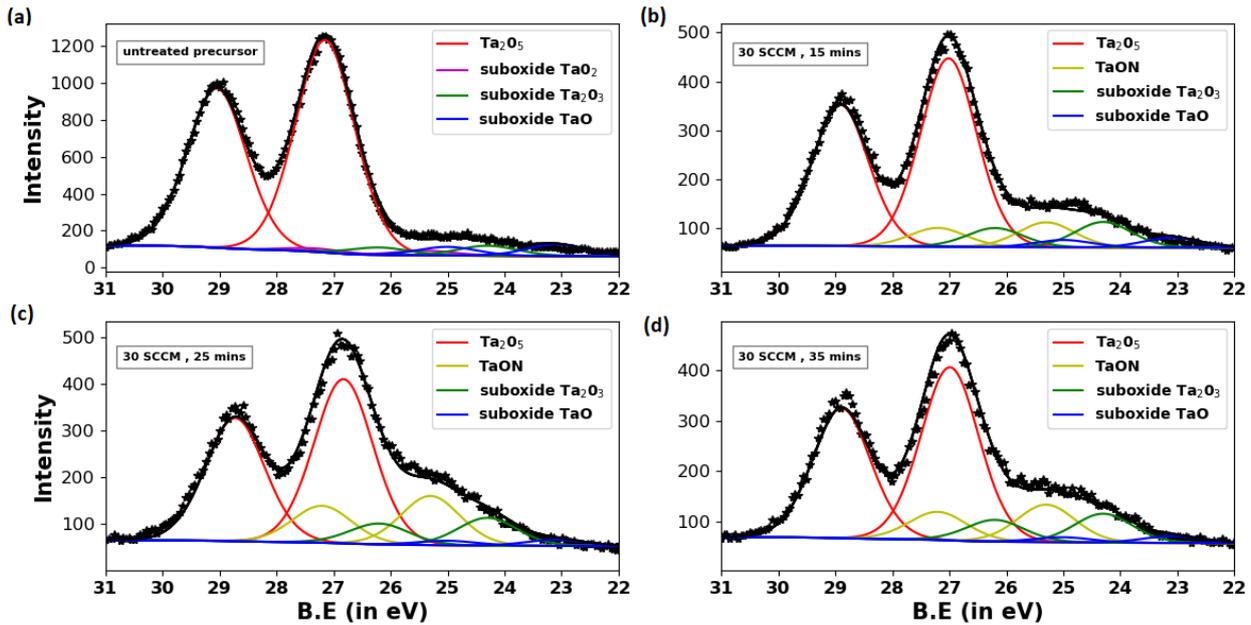


Figure 5: Evolution of Ta 4f spectra with treatment time: (a) Precursor films before APP treatment; Fitted Ta 4f spectra for various treatment times: (b) 15 mins; (c) 25 minutes; (d) 35 minutes. The N₂ feed gas flow rate was kept at 30 sccm. Other parameters: V= 8 kV, Frequency= 2000 Hz.

The evolution of Ta 4f peaks with treatment time is shown in figure 5.

The nitridation pattern with treatment time shows an interesting behavior. As has been said, some parameter combinations yield the formation of substrate oxynitrides (Figure 6) and the main challenge is to get rid of the substrate oxynitride formation. A competition between substrate oxynitride and the surface oxynitrides arise with time. Lower irradiation times (15 minutes) indicate the formation of both Tantalum oxynitrides and substrate oxynitrides. Nitridation of precursor films initially increases with time (at 25 minutes), and the ratio hits a value of 26 % at 25 minutes with the substrate oxynitride ratios going down (from almost 52 % at 15 minutes to 10 %). The Ta oxynitride formation seems to saturate at higher irradiation time of 25 minutes and slightly decreases to 18 % at the treatment time of 35 minutes. The decrease in Tantalum oxynitride formation also bring out a simultaneous increase in substrate oxynitride formation (from 10 % to 14 %) as well. Similar behavior was observed at a flow rate of 20 sccm as well.

Hence a clear competition between precursor nitridation and substrate nitridation arises, and it becomes an extremely challenging problem to choose the desired parameter combinations that would yield the maximum oxynitride formation for films.

Table 2 summarizes the TaON/ Ta oxide ratio obtained for various combination of plasma parameters.

Voltage (kV)	Frequency (Hz)	N ₂ flow rate (SCCM)	Irradiation time (min)	TaON / Ta oxides (%)
8	2000	20	15	5.62
8	2000	20	25	8.63
8	2000	20	35	7.99
8	2000	30	15	11.27
8	2000	30	25	25.94
8	2000	30	35	17.95

Table 2: TaON/ Ta oxide ratio obtained for different set of APP parameters

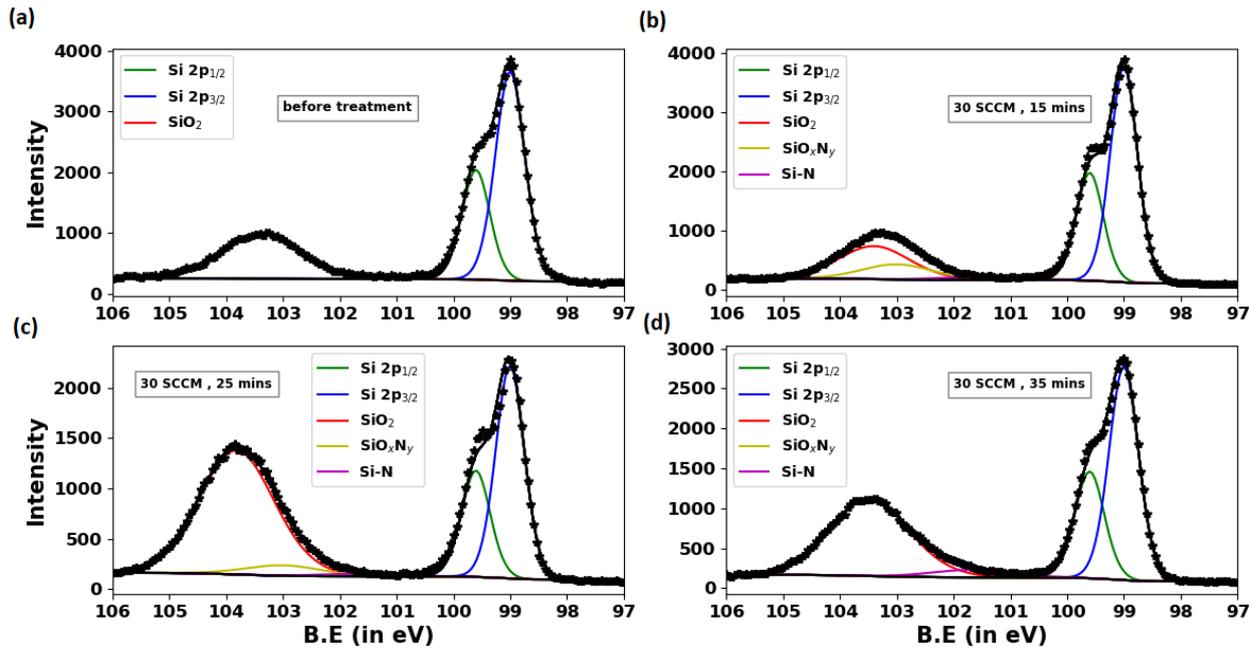


Figure 6: Effect of treatment time on the substrate oxynitridation. Deconvoluted Si 2p spectra obtained ;(a) Before plasma treatment; (b) Treatment time of 15 minutes; (c) Treatment time of 25 minutes; (d) Treatment time of 35 minutes

5 Discussion and future plans

The observed changes in the surface chemistry of the treated precursor films with modulation of APP parameters hint toward alternative material processing routes using plasma. The presence of TaON peaks and nitrogen in the XPS spectra promises a novel approach to deposit photocatalytic films efficiently.

But, choosing the optimal deposition conditions for oxynitrides is an extremely demanding procedure as that requires us to do a lot of experiments at various parameter combinations. For example, if we choose four different values for each of the parameter (Voltage, frequency, deposition time, He flow rate, N₂ flow rate), it will give around 1024 possible combinations and it is experimentally exhausting and demanding to perform a huge number of experiments on that scale.

If we can predict the TaON / Ta oxide ratio for an input set of APP parameters, we would be able to know the desired parameter combinations that have to be used to maximize the oxynitride composition. Predictive modeling of oxynitride formation would help us achieve this. Of course, that demands the use of statistical tools and machine learning with sufficient datasets and I would employ such tools for my future studies.

After achieving the desired deposition, investigation with other surface characterization techniques has to be done to get a complete picture of the deposition process.

6 Acknowledgment

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