Metastable orthorhombic $\text{Ta}_3\text{N}_5$ thin films grown by magnetron sputter epitaxy

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Linköping 2022
Cover image

Left: Atomic model of Ta₃N₅ crystal

Right: TEM image of Ta₃N₅/Ta₂O₅/Al₂O₃ stacking
List of included papers

Paper I

Orthorhombic Ta$_{3-x}$N$_{5-y}$O$_y$ thin films grown by unbalanced magnetron sputtering: the role of oxygen on structure, composition, and optical properties


Paper II

Domain epitaxial growth of Ta$_3$Ns film on c-plane sapphire substrate


Contribution

All papers included in this publish list, I planned and performed the samples growth experiments. The XRD, OES, and OAS characterization instruments were used by me. I analyzed the results and made the plots in the papers.
Abstract

The semiconductor tritantalum pentanitride (Ta$_3$N$_5$) is a promising green-energy material for photoelectrolyzing water to produce oxygen and hydrogen owing to its proper bandgap of $2.0 \pm 0.2$ eV and band positions to redox potential of water. Compare with the conventional setup of water splitting, such as TiO$_2$, Fe$_2$O$_3$, Cu$_2$O, and WO$_3$, the Ta$_3$N$_5$ shows a proper band gap, which leads to a theoretical efficiency as high as 15.9%. However, the complexity of the Ta-N system and the metastability of the Ta$_3$N$_5$ result in the limited research of the growth of high quality stoichiometric Ta$_3$N$_5$.

Conventionally, the two-step growth of oxidation and nitridation of a metal Ta using thermal annealing in oxygen and ammonia environment is used to produce the Ta$_3$N$_5$. However, the amount of incorporated oxygen in the Ta$_3$N$_5$ samples and film’s thickness and interface are hardly to be controlled, and the use of ammonia as the nitridation gas is harmful to the environment. Hence, in this thesis work, the reactive magnetron sputtering is used to synthesis the Ta$_3$N$_5$, which demonstrates some advantages, such as possibility to grow on a substrate with nanostructure on the surface, a simplification of growth process, usage of environmental-friendly reactive gas, and even scaling up to the industrial application.

The thesis presents a successful growth of orthorhombic Ta$_3$N$_5$-type Ta-O-N compound thin films on Si and sapphire substrates, specifically Ta$_{3-x}$N$_{5-y}$O$_y$, using reactive magnetron sputtering with a gas mixture of Ar, N$_2$, and O$_2$. In the deposition process, the total working pressure was increasing from 5 to 40 mTorr, while keeping same partial pressure ratio (Ar: N$_2$: O$_2$ = 3: 2: 0.1). When the total pressure in the region between 5-30 mTorr, a low-degree fiber-textural Ta$_{3-x}$N$_{5-y}$O$_y$ films were grown. In addition, with the characterization of elastic recoil detection analysis (ERDA), the atomic fraction of O, N, and Ta of as-grown Ta$_{3-x}$N$_{5-y}$O$_y$ films were found varying from 0.02 to 0.15, 0.66 to 0.54, and 0.33 to 0.31, respectively, which leads to a $b$-lattice constant decrease around 1.3 %, shown in X-ray diffraction (XRD) results. For a total working pressure up to 40 mTorr, an amorphous O-rich Ta-O-N compound film was formed mixed with non-stoichiometric TaON and Ta$_2$O$_3$, which further raised the oxygen atomic fraction to ~0.48. The increasing total working pressure results in an increasing band gap from 2.22 to 2.66 eV of Ta$_{3-x}$N$_{5-y}$O$_y$ films, and further increasing to around 2.96 eV of O-rich Ta-O-N compound films. The mechanism of increasing oxygen atomic fraction in the film is founded correlated with the forming oxide on the Ta target surface during the deposition process due to the strong reactivity of O to Ta by the characterization of optical emission spectroscopy (OES). Moreover, the sputter yield was reduced
due to the target poisoning, and which is evidenced by both plasma analysis and depth profile from ERDA.

A further studies with the deposition parameters for nearly pure Ta$_3$N$_5$ films (oxygen atomic fraction ~2%) was performed using c-axis oriented Al$_2$O$_3$ substrate. In this research, it is found that a Ta$_2$O$_5$ seed layer and a small amount of oxygen were necessary for the growth of Ta$_3$N$_5$. Without the help of seed layer and oxygen, only metallic TaN phases, either mixture of $\varepsilon$- and $\delta$-TaN or $\delta$-TaN were grown, evidenced by X-ray photoelectron spectroscopy (XPS). Furthermore, the structure and phase purity of Ta$_3$N$_5$-phase dominated films was found highly correlated with the thickness of the Ta$_2$O$_5$ seed layer. With the increasing thickness of the seed layer from 5, 9, to 17 nm, the composition of grown films was changed from 111-oriented $\delta$-TaN mixed with c-axis oriented Ta$_3$N$_5$, c-axis oriented Ta$_3$N$_5$, to polycrystalline Ta$_3$N$_5$. In addition, the azimuthal $\phi$-scans in grazing incident geometry demonstrates that the c-axis oriented Ta$_3$N$_5$ contained epitaxially three-variant-orientation domains, in which the $a$ and $b$ planes parallel to the $m$ and $a$ planes of c-axis oriented Al$_2$O$_3$. With the simulation of density functional theory (DFT), the growth of thin seed layers of orthorhombic Ta$_2$O$_5$ ($\beta$-Ta$_2$O$_5$) was found promoting by introducing a small amount of oxygen, after calculating the interplay between the topological and energy selection criteria. By the co-action of the mentioned criteria, this already grown Ta$_2$O$_5$ seed layer favored the growth of the orthorhombic Ta$_3$N$_5$ phase. Hence, the mechanism of the domain epitaxial growth of c-axis oriented Ta$_3$N$_5$ on c-axis oriented Al$_2$O$_3$ is attributed to the similar atomic arrangement Ta$_3$N$_5$(001) and $\beta$-Ta$_2$O$_5$(201) with a small lattice mismatch around of 2.6% and 4.5%, for the interface of film/seed layer and seed layer/substrate, respectively, and a favorable energetic interaction between involved materials.
Halvledaren tritantalpentanitrid (Ta$_3$N$_5$) är ett lovande grönenergimaterial för fotoelektrolysering av vatten för att producera syre och väte på grund av dess rätta bandgap på 2,0 ± 0,2 eV och bandpositioner till vattens redoxpotential. Jämfört med den konventionella anordningen för vattenklyvning, såsom TiO$_2$, Fe$_2$O$_3$, Cu$_2$O och WO$_3$, visar Ta$_3$N$_5$ ett korrekt bandgap, vilket leder till en teoretisk effektivitet så hög som 15,9%. Komplexiteten hos Ta-N-systemet och metastabiliteten hos Ta$_3$N$_5$ resulterar emellertid i begränsad forskning om tillväxten av högkvalitativa stökiometrisk Ta$_3$N$_5$-filmer.

Konventionellt används en tvästegs metod genom oxidation och nitridering av Ta-metall för att producera Ta$_3$N$_5$, med hjälp av termisk glödning i syre- och ammoniakmiljö. Mångden inkorporerat syre i Ta$_3$N$_5$-proverna, filmens tjocklek och gränsytan mellan metall och film kan sällan kontrolleras, och användningen av ammoniak som nitrideringsgas är skadlig för miljön. I detta examensarbete används därför reaktiv magnetronsputtering för att syntetisera Ta$_3$N$_5$, vilket har flera fördelar såsom förenklande av tillväxten, möjlighet att växa på ett substrat med nano-strukturerad yta, användning av miljövänlig reaktiv gas, och även god skalbarhet för industriell tillämpning.

Avhandlingen presenterar en framgångsrik tillväxtmetod av ortorombiska Ta$_3$N$_5$-typ Ta-O-N sammansatta tunna filmer, specifikt Ta$_{3-x}$N$_5$O$_x$, på Si- och safirsubstrat genom reaktiv magnetronsputtering med en gasblandning av Ar, N$_2$ och O$_2$. I tillväxtprocessen ökade det totala arbetstrycket från 5 till 40 mTorr, samtidigt som partialtrycksförhållande bibehölls (Ar: N$_2$: O$_2$ = 3: 2: 0,1). När det totala trycket låg mellan 5-30 mTorr, växte Ta$_{3-x}$N$_5$O$_x$ filmen med en lågvärdig fiber-textur. Dessutom, genom karacterisering med ERDA, sågs att kvoten (per atom) av O, N och Ta i Ta$_{3-x}$N$_5$O$_x$ -filmerna som växte varierande från 0,02 till 0,15, 0,66 till 0,54 respektive 0,33 till 0,31, vilket leder till en minskning av b-gitterkonstanten runt 1,3 %, som visas i XRD-resultaten. Vid ett totalt arbetstryck upp till 40 mTorr bildades en amorf O-rik Ta-O-N-sammansättning blandad med icke-stökiometrisk TaON och Ta$_2$O$_5$, vilket ytterligare höjde syrekvoten till ~0,48. Ett ökande totalt arbetstryck resulterar i ett ökande bandgap från 2,22 till 2,66 eV för Ta$_{3-x}$N$_5$O$_x$ -filmer och en ytterligare ökning till cirka 2,96 eV för O-rika Ta-O-N-sammansatta filmer. Mekanismen för ökande bråkdel syreatomer i filmen karacteriseras med hjälp av OES och korreleras med oxidem som bildas på Ta-target under sputtringsprocessen på grund av den starka reaktiviteten av O till Ta. Dessutom reducerades sputterhastigheten på grund av target-förgiftning, vilket bevisas av både plasamaanalys och djupprofiler från ERDA.
Ytterligare studier av sputtringsparametrar för nästan rena Ta₃N₅-filmer (syrekvot ~2%) utfördes med c-Al₂O₃-substrat. I denna undersökning har det visat sig att ett Ta₂O₅-initiallagr och en liten mängd syre var nödvändiga för tillväxt av Ta₃N₅. Utan hjälp av initiallager och syre växtes endast metalliska TaN-faser, antingen en blandning av ε- och δ-TaN eller δ-TaN, vilket framgår av X-ray Photoelectron Spectroscopy (XPS). Dessutom visades att strukturen och fasrenheten hos Ta₃N₅-fasdominerade filmer är starkt korrelerade med tjockleken på Ta₂O₅-initiallagret. Med ökande tjocklek på initiallagret från 5, 9, till 17 nm ändrades sammansättningen av filmerna från 111-orienterad δ-TaN blandat med c-orienterad Ta₃N₅, c- orienterad Ta₃N₅, till polykristallin Ta₃N₅. Dessutom visar azimutala φ-svepningar vid en XRD-geometri med liten infallsvinkel att den c-orienterade Ta₃N₅ innehöll tre varianter av epitaxiella domäner, i vilka a- och b-planen är parallella med m- och a-planen för c-Al₂O₃. DFT simulerings visade att tillväxten av tunna initiallager av ortorombisk Ta₂O₅ (β-Ta₂O₅) främjades genom att introducera en liten mängd syre, efter att ha beräknat samspelet mellan de topologiska- och energi-kriterierna. Genom samverkan av de nämnda kriterierna gynnade de Ta₂O₅-initiallagren tillväxt av den ortorombiska Ta₃N₅-fasen. Därför tillskrivs mekanismen för domänens epitaxiella tillväxt av c-Ta₃N₅ på c-Al₂O₃ det liknande atomarrangemangen för Ta₃N₅ (001) och β-Ta₂O₅(201) med en liten gittermissanpassning på runt 2,6 % och 4,5 %, för gränssnittet mellan film INITIALLAGER/substrat och en gynnsam energetisk interaktion mellan inblandade material.
Preface

This licentiate thesis is a part of my PhD research from 2019 in the Nano-materials Science Unit in Thin Film Physics Division at the Department of Physics, Chemistry and Biology (IFM). This work is supported by by Vetenskapsrådet (grant numbers 2018-04198 and 2021-00357), Energimyndigheten (grant number 46658-1), and Stiftelsen Olle Engkvist Byggmästare (grant number 197-0210). The Swedish Government Strategic Research Area in Materials Science on Functional Materials at Linköping University (Faculty Grant SFO-Mat-LiU 2009-00971) is acknowledged for financial support. I have been enrolled in the Graduate school Agora Materiae.

Jui-Che Chang
2022
Acknowledgements

This thesis work has been done as the licentiate thesis of the studies in Science and Technology in Thin Film Physics Division, Department of Physics, Chemistry and Biology (IFM), Linköping University, Sweden.

The three years studies in my PhD life are tired and full of challenges due to each failure and obstacles in the research. However, with the support and help from the following people, this process is also inspiring and full of joy.

First, I would like to thank my main supervisor, Associate prof. Ching-Lien Hsiao, for always discussing the problems with me and giving good suggestion. Besides, from the training of the experiments, data analysis, to writing articles, your guidance is easily to understand which motivates me to progress gradually.

I appreciate my co-supervisor, Prof. Jens Birch about the meaningful discussion and comments of my studies, which gives me a right direction to the work.

Thanks for another co-supervisor of mine, Senior associate prof. Grzegorz Greczynski, always discussing and teaching the knowledge of XPS technique, which make the publication of my papers smoothly.

Thanks for Prof. Lars Hultman and Associate prof. Fredrik Eriksson always revising my papers and providing lots of helpful comments.

Thanks Senior research engineer Mauricio A. Sortica and Prof. Daniel Primetzhofer for the good collaboration of the ion beam analysis in Uppsala.

Thanks Associate prof. Zhangjun Hu for the good collaboration of the optical analysis.

Thanks Associate prof. Gueorgui Kostov Gueorguiev for the good collaboration of the theoretical simulation and analysis.

Thanks for Associate prof. Per Sandström always helping with fixing the problems of instruments. Without you, the work can’t be done.

Thanks for Dr. Babak Bakhit helping me with the XPS operation and teaching me how to use the analysis software.

Also, I would like to thank all of my colleagues and friends in LiU for every pleasant lunches and fikas. With you, my life in LiU becomes wonderful.

I would like to thank my most lovely wife, Tuan-Tuan, Tsai, for your company during those years. You always cheer me up when I am upset and share the happiness with me. Without your support and company, I don’t think I can keep studying in Sweden. I love you.

In the end, I would like to show my appreciation to my family. Your concern and encouragement from Taiwan make me feel powerful on the path of studying and working in Sweden. My dearest parents, Wei-Ming, Chang and Shu-Hua, Du. I first want to thank your support of studying in Linköping University. Also, you always listen to my complaints and give me some useful advice to overcome the obstacles. My dear brother, Wei-Che, Chang, the leisurely chatting with you make my life in Sweden happier. I love you and miss you so much.
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1. Introduction

1.1 Research objective

In this century, the energy crisis attracts more and more attention from the international society. Till now, the nonrenewable fossil fuel is still dominated the energy source, which leads to increasing greenhouse gases and toxic organic particles. Hence, more efforts are contributed to the research in the field of sustainable development, including production of clean and renewable energy source and usage of environmental-friendly energy. As a promising alternative technique is to harvest the solar energy to convert the water to sustainable fuels, hydrogen with high energy density (141MJ/Kg) [1], by electrolysis, so called photoelectrolysis.

Photoelectrolysis could provide, first, conversion of the solar energy to chemical energy, and storage of this energy as gaseous or liquid oxygen and hydrogen or in compounds such as metal hydrides [2]. The technique was first discovered by Akira Fujishima and Kinichi Honda in 1971. [3] In the setup, a TiO$_2$ semiconductor and a platinum electrode were connected and immersed to a water-based electrolyte to produce the hydrogen and nitrogen. However, due to the wide band gap of TiO$_2$ (~3.2 eV), only the light in the ultraviolet region is absorbed, which results in a low efficiency of photoelectrolysis. Therefore, an alternative material, Ta$_3$N$_5$, was presented to raise the efficiency of the water splitting due to the proper band gap and band positions [3-8] with respect to the redox potential of water [9, 10], which leads to a theoretical efficiency as high as 15.9% [11, 12].

This thesis mainly focusses on the synthesis of the crystalline Ta$_3$N$_5$ in the orthorhombic structure using magnetron sputtering technique. The technique is widely used in the industrial field due to the possibility to scale up the grown films and to grow the materials in a low-energy consuming and environmental-friendly way. However, till now, the studies related to the synthesis of Ta$_3$N$_5$ is limited [5, 13-15] due to the metastability nature of the material and the complexity of Ta-N system.

In this thesis, the first objective is to study the mechanism of the growth of Ta$_3$N$_5$ using magnetron sputtering. Furthermore, the deposition process of Ta$_3$N$_5$ can be revised and optimized to improve the quality and crystallinity with the results studied previously. Second objective is to eventually grow an epitaxial Ta$_3$N$_5$ crystal in large scale using magnetron sputtering with the help of suitable substrates or seed layers.
1.2 Research outline

The thesis is separated to two parts, the introduction part, containing four chapters, and collection of the published papers, which are the results of my research. In the first part, the first chapter discuss the Introduction of the research. In chapter two, Background and material, the basic of photoelectrolysis and materials, Ta$_3$N$_5$, was shown. In chapter three, Material growth and characterization technique, the reactive magnetron sputtering, and characterization method used in the research were discussed. Finally, the last chapter, Summary and contribution to the field, demonstrates the results of my research.
2. Background and material

2.1 The water photoelectrolysis

2.1.1 Principle of photoelectrolysis

Photoelectrolysis of water is the water molecules split to hydrogen and oxygen using the energy provided by incident photons. The decomposition from water to gaseous hydrogen and oxygen is an endothermic reaction demonstrated by the formula below.

\[ H_2O + hv \rightarrow H_2 + \frac{1}{2}O_2 \]

The Gibbs free energy difference for the formation is around 237 kJ/mol, which corresponds 1.23 V per electron transferred according to the Nernst equation, [16].

![Figure 1 A schematic of photoelectrolysis.](image)

To utilize the absorbed solar energy, the semiconductor electrode is contact with a water based electrolyte as shown in fig. 1. After applying an internal electric field, electron-hole pair created by incident photons is separated. The formation of the oxygen is due to the migration of the hole to electrolyte and the recombination between holes and HO\(^-\) in the electrolyte side. On the other side, the migration of electrons results in the reduction of H\(_2\)O and the formation of H\(_2\).
2.1.2 Semiconductors for photoelectrolysis

For semiconductors used as an electrode in water splitting process, several criteria, such as proper band gap and band position should be met. Thermodynamically, the band gap should larger than 1.23 eV [2] to trigger the decomposition of the water. However, a higher potential difference, an overpotential of 0.8V, is estimated to be necessary for driving the photoelectrolysis [17]. In addition, the band position of the valence and conduction bands should match the redox potential of water. With those requirements, besides for the conventionally used material, TiO$_2$ [3], other metal oxides such as, Fe$_2$O$_3$, Cu$_2$O [18], and WO$_3$ [19], were used for water splitting due to the generally inexpensive, stable, and easily prepared on a large scale [20]. However, various limitations such as improper band edge positions and large bandgaps for water splitting of these materials lead to a low solar-to-hydrogen efficiency. Hence, in this thesis work, an alternative material Ta$_3$N$_5$, is chosen and discussed in detail.

2.2 Tritantalum pentanitride (Ta$_3$N$_5$)

2.2.1 Ta-N system

Tantalum belongs to transition metals, which provides the variation of the oxidation states and possibility to form compounds over large non-stoichiometric ratio. Hence, in Ta-N binary system, except for the pure tantalum phase (α and β) and Ta(N) solid solution, nine crystalline tantalum nitride phases are shown in the Table 1 below. The pure tantalum mostly crystallized in body-center-cubic (BCC) structure, so called α-Ta, with a lattice constant around 3.3 Å [21,22]. In addition, pure tantalum crystalized in face-center-cubic (FCC) when α-Ta is deformed, or deposited on heated substrate [23]. In the research of L. Gladczuka et al., another pure tantalum phase, β-Ta, was in a tetragonal structure [22]. With the excess introduction of nitrogen atoms around 5 atomic percentage (at. %) [24], the Ta(N) solid solution forms instead of pure tantalum with interstitial nitrogen atoms. While further increasing the at. % of nitrogen atoms, the Ta-N phases transform from Ta(N), Ta$_4$N, Ta$_2$N to 1:1 stoichiometric TaN phase.

At high nitrogen at. % condition, the two most stable phases, rock salt (NaCl type) δ-TaN and hexagonal (CoSn-type) ε-TaN, are dominated in elevated temperature region [25]. The δ-TaN is a high-temperature, high-pressure phase, which can accommodate excess nitrogen atoms far beyond its stoichiometry [26], shown in this research. (The nonstoichiometric δ-TaN is accompanied by Ta vacancies [27] of TaN$_x$ thin films when x is higher than one.) When the nitrogen at. % over the tantalum at. %, four tantalum nitride phases with higher order exist (cubic Ta$_2$N$_3$, orthorhombic
Ta₃N₅, tetragonal Ta₄N₅ and hexagonal Ta₅N₆). Most of the high order tantalum nitride phases were identified as metallic compound, except for the semiconductor Ta₃N₅ phase.

Table 1: A summary of known Ta-N binary phases.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Chemical formula</th>
<th>Crystal structure</th>
<th>Lattice constant (Å)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Ta</td>
<td>Ta</td>
<td>BCC (FCC)</td>
<td>a = 3.306-3.311</td>
<td>[21, 22]</td>
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<tr>
<td>β-Ta</td>
<td>Ta</td>
<td>Tetragonal</td>
<td>a = 10.194, c = 5.313</td>
<td>[22]</td>
</tr>
<tr>
<td>Ta(N) (Solid solution)</td>
<td>TaN₀.₀₅-TaN₀.₁</td>
<td>BCC Cubic</td>
<td>a = 3.369</td>
<td>[28], [24, 29]</td>
</tr>
<tr>
<td>Ta₂N</td>
<td></td>
<td>Orthorhombic</td>
<td></td>
<td>[30]</td>
</tr>
<tr>
<td>γ-TaN (or γ-Ta₂N)</td>
<td>TaN₀.₄₋₀.₅</td>
<td>HCP (ε-Fe₂N type)</td>
<td>a = 3.041-3.048, c = 4.907-4.919</td>
<td>[31, 32]</td>
</tr>
<tr>
<td>δ-TaN</td>
<td>TaN₀.₉₉-TaN</td>
<td>FCC (NaCl type)</td>
<td>a = 4.336, a = 4.32</td>
<td>[33], [34], [35]</td>
</tr>
<tr>
<td>ε-TaN</td>
<td>TaN₁.₀₀-TaN₁.₀₀</td>
<td>Hexagonal</td>
<td>a = 5.185, c = 2.908, a = 5.188, c = 2.903</td>
<td>[21], [22]</td>
</tr>
<tr>
<td>θ-TaN</td>
<td>TaN₁.₀₀</td>
<td>Hexagonal (WC structure)</td>
<td>a = 2.936, c = 2.885</td>
<td>[36], [37]</td>
</tr>
<tr>
<td>Ta₂N₃</td>
<td>Ta₂N₃</td>
<td>Cubic (La₂O₃-type)</td>
<td>a ≈ 9.8</td>
<td>[38]</td>
</tr>
<tr>
<td>Ta₃N₅</td>
<td>Ta₃N₅</td>
<td><em>Orthorhombic (Fe₃TiO₅-type) (pseudobrookite)</em></td>
<td>a = 3.886, b = 10.212, c = 10.262</td>
<td>[39]</td>
</tr>
<tr>
<td>Ta₄N₅</td>
<td>Ta₄N₅</td>
<td>Tetragonal</td>
<td>a = 6.835, c = 4.272</td>
<td>[22]</td>
</tr>
<tr>
<td>Ta₅N₆</td>
<td>Ta₅N₆</td>
<td>Hexagonal (Nb₅N₆-type)</td>
<td>a = 5.175, c = 10.307</td>
<td>[31, 40]</td>
</tr>
</tbody>
</table>

*Note: Ta₃N₅ refers to the orthorhombic form with pseudobrookite structure.*
2.2.2 Ta₃N₅ crystal structure and electrical properties

The fig. 2 (a), (b) and (c) demonstrate the atomic arrangement of a-plane, b-plane, and c-plane of Ta₃N₅ crystal structure, in which the golden spheres represent to Ta atoms and blue spheres represent to N atoms. The Ta₃N₅ crystal is in an orthorhombic structure with space group CmCm. Ta₃N₅ crystal with pseudobrookite (Fe₂TiO₅) structure is composed of irregular octahedra TaN₆ components with both three and four coordinate nitrogen atoms [41], which allows an increasing accommodation of N atoms [9]. The structure of this material reported in the previous studies contains some confusion due to the small difference around 0.05 Å of the b- and c- lattice constant. Hence, in some literatures, Ta₃N₅ was identified as a tetragonal structure [28]. The structure and lattice parameter proposed in this research in Table. 1. was confirmed using powder neutron diffraction (PND) obtained by Brese et al. [39].

Ta₃N₅ is one promising semiconductor for the water splitting using solar energy with a proper energy gap of 2.0 ± 0.2 eV [4-8] and suitable band positions with respect to the redox potential of water [9, 10]. Nevertheless, the metastability of the Ta₃N₅ contributes to the difficulty of the formation of the Ta₃N₅ phase [42] experimentally. Therefore, the previous studies were limited to the polycrystalline and amorphous Ta₃N₅. However, with the research of theoretical aspect, using density functional theory (DFT) calculation by screened non-local hybrid HSE06 functional, the Ta₃N₅ slabs of different orientation show different redox features and carrier mobility [43]. The studies indicate that the (110) and (001) orientations of Ta₃N₅ crystal are suitable for H₂ evolution reactions (HER), and the (010) orientations of Ta₃N₅ crystal are suitable for O₂ evolution reactions (OER). The difference is due to the different coordination number of the exposed species and their structural arrangement [43]. Moreover, the different surface orientations vary the band gap due to...
the generation of the various surface states near the valence and conduction band maximum (VBM and CBM) by the difference of the number and energetics of the dangling bonds on the surface. Hence, in this thesis work, we focus on not only the formation of polycrystalline Ta₃N₅ but also epitaxial growth of Ta₃N₅.

2.2.3 Ta₃N₅ synthesis

2.2.3(a) Conventional two-step process of oxidation and nitridation

Conventionally, the Ta₃N₅ is mostly prepared by a two-step process of oxidation and nitridation with many variation procedures for each step but keeps the same basic principle [4, 41]. The first step is to prepare Ta-O compound (Ta₂O₅) to obtain the Ta 5+ ions by oxidizing the metallic Ta in the form of powder or thin film. Subsequently, the tantalum oxide was annealed at high temperature in a nitrogen-contained gas (NH₃) to form the Ta₃N₅ phase. Without first oxidation step, the formation of Ta₃N₅ directly from metallic Ta seems to be impossible.

This technique is well researched due to the broad window of the growth condition and the possibility to grow stoichiometric Ta₃N₅. However, the usage of ammonia gas, which may be harmful to the environment, is unavoidable. Also, the amount of incorporation oxygen in the grown films is hard to control. The excess incorporation oxygen atoms may affect the electrical and optical properties which result in worse performance of the water splitting. In addition, to improve the performance of the water splitting, such as a good compromise between absorption and charge carrier recombination, the thickness of the grown films is critical. However, it is difficult to achieve the accurately control of the thickness of the Ta₃N₅ layer and the sharp interface between the Ta₂O₅ and Ta₃N₅ [4, 44] by this preparation method.

2.2.3(b) Atomic layer deposition

To simplify the two step process to directly growth process, an alternative technique, atomic layer deposition (ALD) is used. ALD is a deposition technique for thin film growth in the chemical...
vapor deposition (CVD) class, based on the use of a chemical process in gas phase. Two or more chemical precursors were used in the majority of ALD reactions. The precursors react with the surface of the material (substrate/interlayer) one at a time in a self-limiting manner, sequentially. In ALD process, a thin film is deposited through a repeated exposure of separated precursors, as shown in fig. 3.

ALD deposition of TaN$_x$ has previously been reported using various precursors providing tantalum component. The most used precursors including tantalum halide, such as TaF$_5$ [45], TaCl$_5$ [46,47], and TaBr$_5$ [48]. The Ta$_3$N$_5$ films were deposited using sequential pulses of tantalum halide precursors as a source of tantalum with the co-reactant, anhydrous ammonia. The purified N$_2$ was used as the carrier gas. The deposition process takes place at lower temperature ($\leq$600°C) comparing with the reactive magnetron sputtering. The ALD technique provides a possibility to the synthesis of non-oxide materials with controllable thickness and composition in an oxygen-free atmosphere. However, the unavoidable usage of the chemicals which are harmful to the environment is one disadvantage of this process. In addition, compare to the physical vapor deposition (PVD) technique, such as sputtering, the deposition yield is much slower, which leads to a slow speed of growth rate and a difficulty to use in the industrial field.

2.2.3(c) Reactive magnetron sputtering

Magnetron sputtering is another alternative direct growth technique which overcomes the drawbacks of the two-step process of oxidation and nitridation above, used in this thesis work. The mechanism and process detail of the deposition technique and system are discussed in the section below.

The previous studies demonstrate a direct-growth Ta$_3$N$_5$ film using a gas mixture of nitrogen (N$_2$), argon (Ar) and oxygen (O$_2$) as reactive gas in the sputtering process [5, 13-15]. The oxygen incorporation can be controlled more precisely by tuning the amount of the oxygen gas flow and the gas pressure than the two-step process of oxidation and nitridation. Also, the thickness and the interface of the film can be controlled by adjusting the deposition time of the sputtering process. Besides, the magnetron reactive sputtering technique demonstrates several more advantages, such as growth on nanostructured substrates, hetero-growth of multilayers, usage of environmentally friendly reactive gases, and has potential to scale up for industrial production.

However, the grown Ta$_3$N$_5$ films contain more defects and excess interstitial nitrogen atoms using sputtering technique, which need to be improved.
2.3 Thin film growth mechanism

2.3.1 Nucleation and Growth of sputtering

The fundamental nucleation and growth process on the substrate surface, while the sputtered species reaching the substrate from the target in the sputtering deposition, is shown in the fig. 4. The sputtered species first reach and stick on the substrate surface, and further thermally accommodated (physically adsorbed) with the atoms of the substrate surface. The adsorbed atoms later diffuse on the surface to the energetic favorable sites, which is dominated by the temperature of the substrate and the kinetic energy of the adatoms. During the diffusion, the desorption occurs when the kinetic energy of the adatoms is enough to overcome the binding energy between adatoms and surface. Without the desorption, the diffused adatoms eventually interact with other adatoms and form a small metastable cluster. To minimize the total surface energy, the cluster growth occurs after reaching a critical cluster size. The growth of the metastable cluster includes the adatom-cluster and cluster-cluster interaction. Finally, the growth of the clusters decreases the distance between clusters and provides the possibility to the coalescence of the clusters, which further leads to the formation of a continuous film.

![Figure 4 A schematic of film growth mechanism](image)

2.3.2 Epitaxial growth

Epitaxy, or epitaxial growth, is the growth of a thin crystalline layer, where the atoms follow the arrangement of the substrate in the growing layer using a single crystalline substrate [49]. Also, the epitaxial growth can be seen as an extended growth of a single-crystalline on the top of another layer. To fulfill the epitaxial growth, the alignment with the substrate crystal structure of the deposited materials should be energetic favorable, which usually occurs when the lattice
parameters of deposited layer match the substrate. The difference of the lattice parameter, so called the lattice mismatch ($\varepsilon$), is defined by the formula below,

$$\varepsilon = \frac{a_s - a_f}{a_f},$$

where $a_i$ and $a_s$ represents to the lattice constant of the film and substrate. The epitaxial growth requires a lattice mismatch of less than 15% [50].

Two types of epitaxial growth, homoepitaxy and heteroepitaxy, are widely applied in thin film technology. Homoepitaxy is an epitaxial growth that a crystalline film is deposited on a film or substrate with same materials, in which the lattice mismatch should equal to zero. For instance, Si grown on the pure Si substrate, or GaN grown on high quality GaN films [51, 52]. Another type of epitaxy, heteroepitaxy, is an epitaxial growth that a crystalline film is deposited on a film or substrate with different materials, such as GaN and InAlN on AlN and Ta$_2$N$_2$ on Ta$_2$O$_5$ [53, 54].

In heteroepitaxial growth, besides for the lattice mismatch, the difference of thermal coefficient and chemical properties between deposited materials and substrate also affect the epitaxial growth. In addition, with increasing lattice mismatch of heteroepitaxial growth, the strain generated from the interface of deposited layer and substrate starts to accumulate, which results in the formation of the defects and eventually destruction of the epitaxial growth.

2.3.3 Thin film growth mode

In epitaxial thin film growth, three growth modes, Frank-Van der Merwe, Volmer-Weber, and Stranski-Krastanov growth mode are shown in fig. 5.

Frank-Van der Merwe growth mode

The Frank-Van der Merwe (FM) growth mode is an ideal growth mode, a 2D (2-Dimensional) layer-by-layer growth, shown in fig. 5 (a). The FM growth mode occurs when the adatoms first diffuse to form a single crystal monolayer on the substrate and then grow uniformly layer-by-layer while more materials deposited. To make the FM growth possible, the interaction of adatoms and...
substrate surface should be stronger than the interaction between adatoms (surface adhesive force is stronger than adatom cohesive force). In addition, a clean surface of the substrate is necessary. The FM growth mode is suitable for most of the application, but unfortunately it is observed for only a very small number of film-substrate combinations [55, 56].

**Volmer-Weber growth mode**

The Volmer-Weber (VW) growth mode is a 3D (3-Dimantional) growth, in which the deposited materials aggregate to form small clusters and coarsen the clusters after more materials deposited. To make the VW growth mode possible, the interaction between adatoms should be stronger than the interaction between adatoms and the surface (adatom cohesive force is stronger than surface adhesive force). In the VW growth mode, all of the aggregated clusters grow simultaneously during the deposition process, which leads to a rough surface, shown in fig. 5 (b).

**Stranski-Krastanov growth mode**

The Stranski-Krastanov (SK) growth mode is an intermediary growth mode containing characteristic of both 2D and 3D growth, shown in fig. 5 (c). In the SK growth mode, the transition from layer-by-layer growth to island growth occurs when the grown films reach the critical thickness. The growth is strongly dependent on the properties, chemically and physically, of materials and substrate, such as surface energy and lattice mismatch. The lattice mismatch or the unfavorable adatom-surface interaction result in the formation of the locally strain or defect, which further transform to a nucleation site of the 3D growth.

**2.3.4 Use of buffer layer**

For the materials growth in practice, some substrates show poor lattice and thermal properties matching. In this growth condition, a huge number of defects were generated from the interface, which highly results in the grown materials containing a polycrystallinity or an amorphous structure. Hence, some reported studies, focus on the relation between different grown materials and substrates combination, provide a possible way to improve the quality of grown films. In addition, an alternative technique for solving the mismatch between grown materials and substrates is to insert an intermediate layer, or so called, buffer layer, seed layer, initial layer, between substrate and grown materials. For example, to grow high quality GaN or InAlN, an AlN seed layer is chosen to prevent the growth of dislocation in the AlN layer and relax the stress [53, 54]. In addition, the seed layer can also stabilize a metastable phase by providing a surface with similar atomic arrangement, such as cubic InN film grown on r-plane Al$_2$O$_3$ substrate with a
nitridated cubic AlN layer [57], and metastable tetragonal TaO$_2$ grown on $c$-axis oriented Al$_2$O$_3$ using a tetragonal NbO$_2$ seed layer [58]. In this thesis work, an introduction of orthorhombic $\beta$-Ta$_2$O$_5$ seed layer demonstrates the importance of seed layer for the growth of Ta$_3$N$_5$ phase and the domain epitaxial structure due to the similar atomic arrangement and a small lattice mismatch around 2.6\% between $\beta$-Ta$_2$O$_5$ and Ta$_3$N$_5$. Also, presence of significant number of dangling bonds at the interface Ta$_3$N$_5$/Ta$_2$O$_5$, may mitigate the impact of the energy criterion, which promotes the growth of Ta$_3$N$_5$. 
3. Material growth and characterization technique

3.1 Reactive magnetron sputtering

Sputter deposition is a kind of PVD technique, which taking place in vacuum system to grow high quality films. The basic mechanism is largely a momentum transfer between the bombarding particles (inert gas ions, such as Ar⁺ or Kr⁺) and the atoms near the target surface [59]. The energy transfer is derived using the formula [60],

\[ A = \frac{m_1 m_2}{(m_1 + m_2)^2} \]

where \( A \) represents the ratio of transferred energy to incident energy, \( m_1 \) and \( m_2 \) represents the mass of bombarding ions and target atoms. The bombarding ions were contributed from the plasma, which generated by applying strong negative voltage to the cathode (target side) after introducing the working gas into the vacuum chamber. After the bombarding ions attracted by the negative potential, the energetic atoms on the target were sputtered out to the anode (substrate side) and deposit on the substrate, which is called sputter deposition, shown in fig. 6 (a).

Except for the pure metal coating, to fabricate the nitride or oxide compound thin coating on the substrate, the compound targets were used in the conventional sputtering process. However, an alternative method, reactive sputtering provides the possibility to produce the compound films using high purity metallic target by introducing reactive working gas, such as nitrogen or oxygen into the sputtering chamber during the process [61,62], shown in fig. 6 (b). Compare with the compound target, the high purity metallic targets are easier to fabricate. In addition, introduction of the gas phase simplifies the storage of a large inventory of coating material [63]. During the reactive sputtering process, the reactive gas atoms or ions interact with the sputtered particles both before contacting with the substrate and during the diffusion onto the surface of substrate. Therefore, reactive sputtering provides a possibility to fabricate a variety of compound coating thin films.
As mentioned above, the traditional sputtering process was successfully performed several decades ago [64]. However, several disadvantages, such as low deposition rate, instability of the plasma due to the low ionization efficiency limit the usage of the technique. In the sputtering process, the interaction between bombarding ions and the atom of the target generates the “sputtered” particles. Meanwhile, the interaction also generates the secondary electrons from the target, which play an important role in maintaining the plasma [65]. Hence, a more advanced alternative, magnetron sputtering technique, is invented to overcome the mentioned disadvantages. The configuration of the magnetron is designed that one pole with cylinder configuration sat on the central axis and second pole with ring configuration sat around the outer edge, shown in fig. 7. The magnetron traps the secondary electrons in a torus above the target, whose movement can be explained by Lorentz force law [66],

\[ F = q(E + V \times B), \]

where E represents to the electric field, V and q represents to the velocity and charge of the moving particles. B represents to the magnetic field, and F represents to the experienced force of the particles. The confined secondary electrons increase the possibility of the collision between electrons and atoms in the plasma, which results in a higher ionization degree. Furthermore, plasma density near the target surface is increased due to the higher ionization degree, which leads to the more frequently bombardment of the ions. Therefore, the sputtering yield is increased, which further increases the deposition rate and decreases the demanded voltage and working pressure to maintain the plasma.

Figure 6 Schematic of principle of (a) sputtering and (b) reactive sputtering
For magnetron sputtering technique, three different types of magnetron configuration are shown in fig. 8.

(a) **Conventional balanced magnetron**

(b) **Unbalanced magnetron type I**

(c) **Unbalanced magnetron type II**

In the conventional balanced magnetron configuration, the strength of the magnets in the middle and on the edge is same. All magnetic field lines start from the magnet on the edge and loop back to the magnet in the middle [32]. Hence, the plasma was well confined to the region near the target surface. This results in low density of plasma when the substrate located around 50 mm far from the target surface [67]. An alternative design, unbalanced magnetron configuration, was designed to overcome the disadvantages. The only difference is the slight weaker strength of
one set of magnet (For Type I configuration, the center pole is stronger than the edge pole. For Type II configuration, the edge pole is stronger than the center pole.) However, the small difference result in a significant improvement due to the unclosed magnetic field lines. The secondary electrons with faster movement follow the unclosed magnetic field lines and expand toward the region near the substrate. The higher electron density provides higher possibility of the interaction between electrons and atoms in the plasma and results in a dense plasma near the substrate. In addition, an extra bias can be applied to increase the number and kinetic energy of the ions in the plasma and attract the ions to the substrate.

The vacuum system for magnetron sputtering used in this thesis was a combination of a sputtering chamber, a transfer tube, and a load lock. The 60 cm-diameter magnetron sputtering chamber equipped with a mechanical pump and a turbomolecular pump maintains the back pressure of 10^{-8} to 10^{-7} mTorr. The samples were transferred from the load lock, with a separated pumping system, to the main chamber through the transfer tube.

The magnetron sputtering machine used in this thesis is called Ragnarök, which equipped with four type-II unbalanced magnetron sources with different metallic targets, such as Al, In, Ti, and Ta. The target used in this research for depositing the tantalum nitride work is a 75 mm-diameter pure Ta target (99.99%). The magnetrons are facing upward, and the samples mounted in the substrate holders are clamped by a manipulator, which is installed on the ceiling of chamber. A heater is installed in the manipulator, which provides the function to heat the substrates up to 1000°C, with a thermal couple used for monitoring the growth temperature. To improve the homogeneity of the grown films, the manipulator can rotate with a speed up to 30 rpm. During the deposition process, the Ar, N\textsubscript{2}, and O\textsubscript{2} gases were injected into the chamber via the mass flow controllers to tune the volume of the gases.

3.2 X-ray diffraction

X-ray diffraction (XRD) is a fundamental and important analytic technique to identify the phase and derive the structural information of crystalline materials. Because the wavelength of incident X-ray is sat in the same magnitude order (0.5~2.5 Å) with the spacing between two crystal plane, the constructive interference pattern of the scattered off x-ray from adjacent planes can be measured and characterized to certain crystal structure. Furthermore, for each diffraction pattern, more information of materials, such as lattice constant, lattice strain, preferring orientation, crystal quality, and even chemical composition is able to be extracted.
The constructive interference of incident X-ray only occurs when the condition corresponds to the Bragg’s relation,

\[ n\lambda = 2d_{hkl}\sin\theta, \]

where \( n \) represents to the order of diffraction, \( \lambda \) represents to the wavelength of the incident x-ray beam, \( d \) represents to the distance between two adjacent planes (d-spacing) of specific miller indices, \( hkl \), and \( \theta \) represents to the angle of the incident beam.

### 3.2.1 0-20 X-ray diffraction measurement

The conventional 0-20 XRD measurement was used to demonstrate the crystallinity and identify the contained phase of grown films. Fig. 10 shows the simplified schematic of operation of 0-20 XRD process, in which, the angle between incident X-ray beam and stage symbolled with \( \theta \) (ω) and the angle between incident beam and diffracted beam symbolled with 2\( \theta \). During the measurement, the incident X-ray beam passing through the monochromator illuminates on the sample, and then the X-ray diffracted from sample through the receiving slit to the detector. In the continuously 0-20 scan mode (used in this research), the detector rotates with 20\( ^\circ \) angle, and sample stage rotates with 0\( ^\circ \) angle, simultaneously. (For different design of instrument, the X-ray source is moveable instead of sample stage.) From the formula of Bragg’s relation, with constant wavelength of incident beam, the 20 value recorded by detector is dependent on the d-spacing of measured sample. After analysis, the 0-20 diffraction pattern is able to be characterized to specific material and further identified to the structure and lattice parameters of the plane parallel to the sample surface (out-plane).
The θ-2θ XRD measurement in this thesis work was performed by a Philips Bragg-Brentano powder diffractometer using Cu-Kα radiation with a wavelength of 0.15406 nm. A scan range of 15° to 60° was used with a step size of 0.03° and a collection time of 2 s/step.

3.2.2 Azimuthal scan (φ-scan) in grazing-incident diffraction

However, for the epitaxial or fiber-texture growth films, the traditional θ-2θ XRD measurement only demonstrates the information along the preferential orientation. To characterize the detail of structural properties, such as crystallinity of in-plane orientation and the symmetry of the grown films, a more advanced XRD instrument equipped with Eulerian cradle is required. With the advanced diffractometer, the sample stage is allowed to move not only on the X-Y surface, but also along Z-axis. In addition, the design provides the possibility to rotate the sample stage along the orientation perpendicular to the surface, so called φ-axis, and to tilt the surface of the sample along ψ-axis, shown in fig. 11.
Azimuthal scan, or so called ϕ-scan, is an analysis method to measure the single and derive the information from the crystal plane, which is not parallel to the sample surface. The results were recorded along rotating ϕ-axis, while keeping the same θ, 2θ, and ψ value to match the Bragg’s relation of specific crystal plane. Furthermore, the advanced X-ray diffractometer provides a possibility to make a scan with constant θ and 2θ value, while mapping with changing ϕ and ψ value, so called pole figure. In azimuthal scan, the results identify that the grown films belong to epitaxial, domain epitaxial or fiber-texture growth. In addition, from the amount and the separation degree of peaks from the ϕ-scan patterns, the symmetry of the grown crystal can be defined. For instance, a crystal with a 3-fold symmetry shows three peaks separated with 120° to each other for the ϕ-scan pattern.

In grazing-incident diffraction (GID) geometry, the samples were tilted along the ψ-axis to the angle between 89 to 90°, shown in fig. 12. In this configuration, the information of planes perpendicular to the out-plane can be recorded. Furthermore, after analyzing the measurement in GID geometry of both grown films and substrate, the configuration of in-plane orientation of the stacking can be identified. However, the GID technique contains a shallow probing volume, which leads to that the measurement can only be done for an epitaxial or domain epitaxial films with high crystal quality.

![Figure 12 A illustration demonstrates the grazing incident geometry.](image)

The azimuthal ϕ-scans were performed in a GID geometry using a PANalytical Empyrean X-ray diffractometer in this thesis work. The parabolic mirror was chosen as the primary optics and a 0.27° parallel plate collimator as the secondary optics. In the ϕ-scan, the scan range was set...
from 0° to 360°, with a 1° step size and a 1 s/step scanning time for the film and a 0.2° step size with 0.5 s/step for the substrate.

3.2.3 Double-crystal X-ray rocking curve measurement

To characterize the crystal quality of the grown epitaxial films, the X-ray rocking curve measurement (XRC, ω-scan) was done using a high resolution X-ray diffractometer setup. In the measuring process, a specific 2θ angle, matching chosen hkl-plane, was fixed, while rocking the samples and changing the angle between incident X-ray and sample surface, ω. In theoretically perfect crystal, only when the ω value equals to the chosen 0 value for specific 2θ condition, Bragg’s relation is matched, and diffracted X-ray can be measured. However, a practically perfect crystal still demonstrates a peak with sharp width due to the broadening from the instrument and the intrinsic width of the materials. In practice of material growth, the defects, such as mosaicity, dislocation, strain between grown films and substrate, and the curvature of the grown films lead to a broadening of the peak in XRC [68, 69]. Furthermore, to quantitatively analysis the crystal quality of the grown films, the full width of half maximum (FWHM) of the measured peak in XRC pattern is related to the dislocation density, shown in the research of C. G. Dunn et al [69]. Nowadays, the FWHM of XRC measurement is widely used to characterize the crystal quality of grown materials for high-quality electronics in industrial and laboratory [70, 71].

3.3 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is an analytical technique used to characterize the chemical properties of materials such as, elemental composition, stoichiometry (~ 5% error bar), chemical states, and density of states in the valence band region with high surface-sensitivity. The basic principle of XPS technique is based on the photoelectric effect that the electrons were ejected from the material surface after illuminated by electromagnetic radiation, such as X-ray. The effect can be described by the equation below,

\[ E_B = h\nu - E_k, \]

where \( E_B \) represents to the binding energy of the electron in the atoms, the \( h\nu \) represents to the energy of the irradiation light, and \( E_k \) represents to the kinetic energy of emitted photoelectrons.
In the XPS operation, the sample is irradiated by an incident X-ray with known energy in an ultra-high vacuum (UHV) condition. As shown in fig. 13, the emitted photoelectrons were collected, and the kinetic energy of photoelectrons was analyzed by a spectrometer through an energy analyzer. The equation applied in the practice is revised to,

\[ E_B^p = hν - E_k - \Phi_{sp} \]

where \( E_B^p \) represents the binding energy of electron relative to the Fermi level, and \( \Phi_{sp} \) represents to the work function of the spectrometer. Each element equips a unique electronic structure, and the emitted electrons contain specific and well-defined energy. Hence, after collecting the electronic spectrum and comparing with the reference database, the elements can be identified. In addition, in the research in the 1958 reported by E. Sokolowski et al., the emitted electrons of the same atom with same core-level transition demonstrate different kinetic energy due to the chemical environment difference \[72\], which provides the possibility to distinguish the containing phase of a grown compound sample from analyzing the collected XPS spectrum. For instance, in this research, the binding energy of Ta 4p core-level shows an energy difference around 3 eV, for tantalum nitride and tantalum oxide.

The XPS measurement was performed using a Kratos Axis Ultra DLD instrument with monochromatic Al Kα radiation (\( hν = 1486.6 \) eV) and the software casaXPS was used for data analysis in this research. The measurement was first performed by a low resolution survey scan before a high resolution scan with an analyzer pass energy set to 20 eV, which results in a full width at half maximum of 0.55 eV for the Ag 3d_{5/2} peak. XPS spectra were collected from a 0.3 x 0.7 mm² area in the center of the sample with electrons emitted along the surface normal. The spectrometer was calibrated according to ISO standards \[73\]. The spectra were referenced to the Fermi edge cut-off \[74\] to avoid uncertainties associated with using the C 1s peak of adventitious
carbon for that purpose [75]. The peak shifts owing to charging effect was shown in the spectra recorded from films on the insulator substrates, which was compensated using a spectrum of films on Si substrate. The quantification was performed based on peak areas and elemental sensitivity factors from Kratos Analytical Ltd.

3.4 Elastic recoil detection analysis

The heavy ions time-of-flight elastic recoil detection analysis (TOF-ERDA) is a promising technique used to analyze the chemical composition, especially for light elements, such as N, O and C in a heavy atom’s matrix. The samples were projected by a heavy ions beam, and the elastic interaction between the incident ion beam and the atoms of the samples occurs. Depth information is extracted by the energy loss of projectile and recoil ions in the sample. Meanwhile, the yield of recoils measured with a certain energy reveals the sample composition in a certain depth [76]. However, in the conventional ERDA configuration, the measurement of mass of recoil atoms or ions and the scattering depth served with high difficulty. Hence, an alternative configuration shown in fig. 14, ERDA with ToF spectrometry, in which the mass of the particles is determined by the coincident measurement of its velocity [77] to distinguish the mass of different atoms.

A primary beam of iodine ions with an energy of 36 MeV was used in the experiments in this thesis work. The measurements were carried out at a recoil detection angle (φ) equal to 45° with respect to the primary beam and a target angle (β) equal to 22.5° with respect to the sample surface, using a 0.425 m effective length of the time-of-flight distance. Since the accuracy of the results decreases with increasing depth due to multiple scattering effects in ERDA, the analyzed data was averaged in the depth region 50 - 200·10^{15} atoms/cm² for δ-TaN sample and 50 - 500·10^{15} atoms/cm² for Ta-O-N compounds samples. The concentration ratios (atomic fraction) are less affected by the by systematic uncertainties than absolute concentrations. This trend allows to compare the concentrations for different samples. A detailed discussion of possible systematic uncertainties can be found in the research before [78].

Figure 14 A schematic of ERDA measurement.
3.5 Optical emission spectroscopy

Optical emission spectroscopy (OES) is a technique widely used in plasma studies to determine the radiative deexcitation of atomic, molecular, and ionic states. The deexcitation between different energy level in the discharge plasma generates photons with specific energy, which results in the unique spectrum for each element. In the reactive sputtering process, the discharge plasma containing several different particles, such as metal ions, reactive gas atoms, and molecules etc., in which the illuminated light can be considered as combination of the numerous characteristic emission spectral lines. To analyze discharge plasma, the emitted light was collected and focus to the spectrometer through an optical fiber. To split the light from different species, a diffraction grating was used to distinguish the mixed incident beam to light with element-specific wavelengths before reaching the spectrometer. The detector measures the intensity of each light and transport the data to computer system to analyze with a predefined calibration by known element. The instrument setup is shown in the fig. 15.

![Figure 15 A schematic of OES measurement.](image)

The OES Instrument used in this thesis to characterize the plasma during sputtering is Ifu Diagnostic Systems GmbH AOS 4-1 μchron 02. Before the measurement, the instrument was calibrated using the spectrum of neon. The emitted photons from the plasma were collected by an optical fiber to OES and sent to the spectrometer via a viewport in the chamber. The scanning range was set to 400 - 800 nm and a 1-nm step size was used, due to the absorption of the photons
with wavelength shorter than 400 nm by the viewport. The collection time for each step was 0.01 s and the voltage to the photo multiplier tube (PMT) was set to 1000 V.

### 3.6 Optical absorption spectroscopy

Optical absorption spectroscopy (OAS) is a technique used to determine the chemical, atomic, and molecular composition of present sample. In addition, for samples with known constitute materials and composition, the technique provides the possibility to characterize the optical and electrical properties, such as absorption coefficient and energy edge. The principle of the OAS is to measure the radiation absorption of materials as a function of wavelength or frequency due to the interaction between the incident phonons and samples. When the incident radiation matches the specific energy difference between quantum states, the phonons are absorbed and the electron transition between two states occurs. The absorption varies with changing wavelength and frequency of the incident radiation, whose variation is presented as an absorption spectrum. During the characterization process, an absorption spectrum of blank substrate was first measured as a reference spectrum. After subtracting the absorption spectrum of the samples with spectrum of substrate, the absorption spectrum of measured materials can be determined.

To determine the band gap of the samples using absorption spectrum, the Tauc’s formula, shown below, is used,

$$\omega^2 A(\lambda) = (\hbar \omega - E_g)^2,$$

where $A(\lambda)$ is the absorbance of the materials, $\lambda$ is the wavelength of incident radiation, $\omega = 2\pi v$ is the angular frequency of incident radiation and $E_g$ is the band gap (energy edge). $E_g$ can be deduced to $(A^{1/2} / \lambda)$ versus $(1 / \lambda)$ by Tauc’s formula. Hence, the intersection of the extrapolated line of the spectrum and X-axis give the wavelength $\lambda_g$ of $E_g$.

The Ultraviolet-visible spectrophotometer (Shimadzu, UV-2450) was used in this research for measuring the band gaps of the grown films on sapphire substrates. Due to the smaller band gap of Si (1.1 eV) than $\text{Ta}_{1-x}\text{N}_x\text{O}_y$ (> 2 eV), the photon energy larger than band gap of Si was absorbed, which is not the proper substrate used for this OAS measurement. Herein, the sapphire was used as the substrates and the absorption spectrum of sapphire was measured as background. The spectra were collected in the range of 250-900 nm. The band gaps for the samples were calculated utilizing the Tauc method.
4. Summary and contribution to the field

The results demonstrated in this thesis work focus on the synthesis of $\text{Ta}_3\text{N}_5$ using reactive magnetron sputtering, and growth of domain epitaxial $\text{Ta}_3\text{N}_5$ films with an introduction of $\text{Ta}_2\text{O}_5$ seed layer. The final goal of the research is to successfully synthesis high quality single crystal $\text{Ta}_3\text{N}_5$, which can used to split the water with high stability and efficiency.

In Paper I, an orthorhombic $\text{Ta}_3\text{N}_5$-type $\text{Ta}_{3-x}\text{N}_{5-y}\text{O}_y$ compound films were successfully directly synthesized on Si and sapphire using reactive magnetron sputtering. In addition, the containing N and O atomic fraction varies with different total working pressure range from 5 to 40 mTorr, while keeping the same partial pressure (Ar: $\text{N}_2$: $\text{O}_2$ = 3: 2: 0.1). At the lowest working pressure condition, 5 mTorr, the oxygen atomic fraction is 0.02, which demonstrates a nearly pure $\text{Ta}_3\text{N}_5$. With increasing total working pressure to 30 mTorr, the grown $\text{Ta}_{3-x}\text{N}_{5-y}\text{O}_y$ compound films still maintain the orthorhombic structure with an increasing oxygen atomic fraction up to 0.15 and a decreasing nitrogen and tantalum atomic fraction from 0.66 to 0.54 and 0.32 to 0.31. Meanwhile, the $b$-lattice constant decreases around 1.3 %, and the band gap increases from the 2.22 to 2.66 eV. The results mentioned indicates the O atoms in the films substituted for N sites and the formation of $\text{Ta}_3\text{N}_5-x\text{O}_y$ compounds. When the working pressure increases up to 40 mTorr, the oxygen atomic fraction dramatically increases to 0.48, and the grown films transformed to a $\text{TaO}_x$ and $\text{Ta}_2\text{O}_5$ mixed phase, proved by XPS and OAS characterization. Moreover, only metallic $\text{TaN}$ compound was found in a deposition with a gas mixture of Ar and $\text{N}_2$ without $\text{O}_2$, which demonstrates that the oxygen plays a critical role in the growth of $\text{Ta}_3\text{N}_5$-structure using magnetron sputtering.

A further study proves that besides for the introduction of oxygen, a $\text{Ta}_2\text{O}_5$ thin seed layer is also necessary for the $\text{Ta}_3\text{N}_5$ growth using magnetron sputtering, shown in Paper II. Without the use of both seed layer and $\text{O}_2$ in reactive gas, the grown compound films only composed by metallic $\text{TaN}$ phase, such as a mixture of $\varepsilon$- and $\delta$-$\text{TaN}$ or pure $\delta$-$\text{TaN}$. In addition, the thickness of the interlayer found strongly affects the grown $\text{Ta}_3\text{N}_5$-phase dominated films. When the seed layer’s thickness increases from 5, 9 to 17 nm, the constitute of grown films changes from a mixture of $\varepsilon$- and $\delta$-$\text{TaN}$ or pure $\delta$-$\text{TaN}$. As a support of DFT simulation, the introduction of an orthorhombic $\text{Ta}_2\text{O}_5$ ($\beta$- $\text{Ta}_2\text{O}_5$) found benefit the growth of $\text{Ta}_3\text{N}_5$, and the
stacking relation of film/seed layer/substrate along in-plane orientations of Ta₃N₅[010], β-Ta₂O₅[1̅02], and Al₂O₃[11̅20] was shown.

With the results mentioned in this thesis work, a high-purity Ta₃N₅ with domain epitaxy was successfully grown using reactive magnetron sputtering. Looking for a more suitable substrate and seed layer is the next step for the research to grow single-crystal Ta₃N₅. In addition, another direction of the research is to further improve the stoichiometry of grown Ta₃N₅, which is planned to achieve using Krypton (Kr) in the working gas, or using the high-power impulse magnetron sputtering (HIPIMS) technique to increase the ionization of the Ta.
Reference


Paper I

Orthorhombic Ta$_{3-x}$N$_{5-y}$O$_y$ thin films grown by unbalanced magnetron sputtering: The role of oxygen on structure, composition, and optical properties

Jui-Che, Chang, Fredrik Eriksson, Mauricio A. Sortica, Grzegorz Greczynski, Babak Bakht, Zhangjun Hu, Daniel Primetzhofer, Lars Hultman, Jens Birch, Ching-Lien, Hsiao

Surface and Coatings Technology, Volume 406, 25 January 2021, 126665

https://doi.org/10.1016/j.surfcoat.2020.126665

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Orthorhombic Ta$_{3-x}$N$_{5-y}$O$_{y}$ thin films grown by unbalanced magnetron sputtering: The role of oxygen on structure, composition, and optical properties

Jui-Che Chang, Fredrik Eriksson, Mauricio A. Sortica, Grzegorz Greczynski, Babak Bakhtia, Zhangjun Huc, Daniel Primetzhofer, Lars Hultman, Jens Birch, Ching-Lien Hsiao

ABSTRACT

Direct growth of orthorhombic Ta$_{3-x}$N$_{5-y}$O$_{y}$-type Ta-O-N compound thin films, specifically Ta$_{3-x}$N$_{5-y}$O$_{y}$, on Si and sapphire substrates with various atomic fractions is realized by unbalanced magnetron sputtering. Low-degree fiber-textural Ta$_{3-x}$N$_{5-y}$O$_{y}$ films were grown through reactive sputtering of Ta in a gas mixture of N$_2$, Ar, and O$_2$ with keeping a partial pressure ratio of 3:2:0.1 in a total working pressure range of 5-30 mTorr. With increasing total pressure from 5 to 30 mTorr, the atomic fraction of O in the as-grown Ta$_{3-x}$N$_{5-y}$O$_{y}$ films was found to increase from 0.02 to 0.15 while that of N and Ta decrease from 0.66 to 0.54 and 0.33 to 0.31, respectively, leading to a decrease in the lattice constant up to around 1.3%. Metallic Ta$_x$N$_y$ phases were formed without oxygen. For a working pressure of 40 mTorr, an amorphous, O-rich Ta-N-O compound film with a high O fraction of ~0.48, was formed, mixed with non-stoichiometric TaON and Ta$_2$O$_5$. By analyzing the plasma discharge, the increasing O incorporation is associated with oxide formation on top of the Ta target due to a higher reactivity of Ta with O than with N. The increase of O incorporation in the films also leads to a optical bandgap widening from ~2.22 to ~2.96 eV, which is in agreement with the compositional and structural changes from a crystalline Ta$_{3-x}$N$_{5-y}$O$_{y}$ to an amorphous O-rich Ta-O-N compound.

1. Introduction

Photoelectrolyzing water into hydrogen and oxygen by renewable electricity is a possible method to produce clean hydrogen. Most conventional setups consist of a semiconducting TiO$_2$ electrode which often shows low efficiency for water splitting [1]. Other oxide semiconductors, such as Fe$_2$O$_3$, Cu$_2$O [2], and WO$_3$ [3] have been studied as photoanodes because of their stability. However, these materials suffer from various limitations such as large bandgaps and improper band edge positions for water splitting. Semiconductor orthorhombic tritantalum pentanitride (Ta$_3$N$_5$) is one of the most promising materials for the photoelectrolysis of water owing to a proper energy gap of 2.0 ± 0.2 eV [4–8] and suitable band positions with respect to the redox potential of water [9,10]. Related, monoclinic and bixbyite tantalum oxynitrides (TaO$_x$N$_y$) and with a bandgap range of 2.4–2.8 eV [5–7,11] and ~2 eV [12], respectively, were also demonstrated to have a good response for water splitting although its valence band energy is lower than Ta$_3$N$_5$. Therefore, the Ta-O-N compounds are promising materials with tunable bandgap and band positions to fit a desired value for the water splitting.

Conventionally, Ta$_3$N$_5$ is produced through a two-step process of oxidation and nitridation of a Ta metal foil. However, the amount of incorporated oxygen in the Ta$_3$N$_5$ samples and film’s thickness are hardly to be controlled [7,13], and the use of ammonia as the nitridation gas is harmful to the environment. It should be noted that regardless of how much oxygen that is incorporated into the films, the chemical formula Ta$_3$N$_5$ is used as a generic name. Direct, single-step, growth of Ta$_3$N$_5$ onto various types of substrates using atomic layer deposition [14,15] and reactive magnetron sputtering are reported [8,16–18], which demonstrates several advantages, such as simplification of the deposition process, growth on nanostructured substrates, and hetero-
growth of multilayers with other potential materials. Moreover, magnetron sputtering has the potential to scale up for industrial production and enabling use of the environmentally-friendly reactive gases argon (Ar), nitrogen (N₂) and oxygen (O₂) to produce high-quality semiconductors [18–21].

To date, studies on the direct growth of Ta₃N₅ are limited in number due to the nature of metastable structures in the complex system of Ta–N binary compounds [22,23]. Direct growth of Ta₃N₅ often results in the formation of stable metallic cubic phases, mostly 6-TaN and c-Ta₃N₅ [22]. Despite that the concentration ratio of N to Ta in sputtered TaₙN films can be higher than 1.67, the film is preferable to be grown in cubic Ta₃N₅ phase with excess N rather than in the orthorhombic Ta₃N₅ phase (x ~ 1.67). Calculations predict that a small number of oxygen atoms incorporated in the film can stabilize an orthorhombic-Ta₃N₅ structure through the electronegativity enhancement induced by the oxygen [24].

M. Rudolph et al. successfully produced polycrystalline Ta₃N₅ films by direct current (DC) magnetron sputtering using a balanced magnetic coil configuration allowing a uniform seeding of a small amount of oxygen in the range of 2–2.5% into the reactive gas [8]. The crystallinity of the sputtered Ta₃N₅ films can be further improved by increasing ion flux to the growing film by using an electromagnetic coil to attract ions to the substrate [16]. Although the direct growth of metallic cubic Ta₃N₅-type film is promising, the study of incorporated oxygen on the control of crystalline structure, chemical composition and bonding, and optical properties of as-grown Ta-O-N films as well as the effect of oxygen in reactive sputtering process is rarely reported [1]. Be specific, more studies on the process control and incorporated oxygen on the materials properties are required for developing the growth high-quality Ta₃N₅ films, such as single crystalline structure and stoichiometry, aiming for application of high efficiency water splitting.

In this work, ultrahigh vacuum (UHV), unbalanced, DC magnetron sputtering (DCMS) [25] was used to deposit Ta₂O₅Nₓ-Oₓ compound films with varying total working pressure to introduce a small amount of oxygen. To illustrate the difference to pure Ta₃N₅ crystals, a chemical formula Taₙ₂N₅Oₓ has been used to present the orthorhombic Ta₃N₅-type Ta₂O₅Nₓ compounds. The UHV condition of the system enables to eliminate possible contribution of oxygen originating from the residual background gas. The use of unbalanced magnetic configuration can guide the plasma towards the substrate resulting in enhancement of knowledge with ion assists, which simplifies the process [26,27]. To study the effects of oxygen on structure, composition, and optical properties of the as-grown films, several characterization techniques were used. The crystalline structure and chemical composition of the as-grown films were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and elastic recoil detection analysis (ERDA). Optical emission spectroscopy (OES) was used to analyze the plasma discharge properties during the reactive magnetron sputtering growth. The energy band gap of the films was determined by optical absorption spectroscopy (OAS). The role of oxygen in the formed Ta₂O₅Nₓ structure, chemical composition and bonding, optical properties, and sputtering process are discussed.

2. Experiments

2.1. Materials growth

The films were deposited on single crystal n-type Si (111) and sapphire Al₂O₃ (0001) substrates using UHV DCMS [28]. Both substrates were deposited at the same time. An unbalanced type-II magnetron configuration was used for guiding the plasma towards the substrate. Before deposition, the substrate was cleaned in ultrasonic baths with acetone and isopropanol ultrasonic baths for 5 min each and dried by blowing nitrogen. The substrate was then loaded in a load lock chamber and transferred to the deposition chamber. A continuous substrate rotation of 30 rpm was applied to ensure a homogeneous film during deposition. First, a thin amorphous TaN₅O₅ seed layer was deposited at room temperature and annealed at 1000 °C to minimize the effect of any substrate surface structure. For the growth of oxygen-free samples, reactive sputter deposition of a 75 mm diameter Ta target (99.5%) using a gas mixture of N₂ and Ar with the partial pressures of 3 and 2 mTorr, respectively, was employed at 800 °C. The magnetron power and deposition time were set to 150 W and 20 min, respectively. For samples grown with oxygen, a partial pressure of 0.1 mTorr oxygen was introduced to the gas mixture with a partial pressure of 3 mTorr N₂ and 2 mTorr Ar, corresponding to ~2% of the total pressure. Keeping the same partial pressure ratio (N₂:Ar:O₂ ~ 3:2:0.1), six samples were deposited at total working pressures of around 5, 10, 15, 20, 30, and 40 mTorr by throttling the main chamber turbopump. All oxygen-containing samples were deposited at 800 °C, for 20 min and the magnetron power was set at 300 W.

2.2. Sample characterizations

Structural property was obtained from XRD 0/20 measurement, performed using a Philips Bragg-Brentano powder diffractometer using Cu-Kα radiation with a wavelength of 0.15406 nm. A scan range of 15° to 60° was used with a step size of 0.02° and a collection time of 2 s/step. XPS analysis of surface chemistry was carried out on a Kratos Axis Ultra DLD instrument employing monochromatized Al Kα radiation (hν = 1486.6 eV). The spectra are referenced to the Fermi edge cut-off [29,30] to avoid uncertainties associated with using the C 1s peak of adventitious carbon for that purpose [31]. The analyzer pass energy was set to 20 eV which resulted in a full width at half maximum of 0.55 eV for the Ag 3d peak. Quantification of the elements in the samples was performed using the Casa XPS software (version 2.3.16), based upon peak areas from narrow energy range scans and elemental sensitivity factors supplied by Kratos Analytical Ltd.

The chemical composition of the films, with a particular focus on light species such as C, N, and O was analyzed by heavy ion time-of-flight ERDA. A primary beam of iodine ions with an energy of 36 MeV was used in the experiments. The measurements were carried out at a recoil detection angle (α) equal to 45° with respect to the primary beam and a target angle (β) equal to 22.5° with respect to the sample surface, using a 0.425 m effective length of the time-of-flight distance. Since the accuracy of the results decreases with increasing depth due to multiple scattering effects in ERDA, the analyzed data was averaged in the depth region 50–200–10⁵ atoms/cm² for 6-TaN sample and 50–500–10⁵ atoms/cm² for Ta₂O₅Nₓ compounds samples. It should be noted that when comparing different samples, concentration ratios (atomic fractions) are less affected by systematic uncertainties than absolute concentrations. This fact allows relying even on weak trends in concentrations for different deposition conditions. A detailed discussion of possible systematic uncertainties can be found elsewhere [32].

AES was performed to characterize the plasma during sputtering using a Bio Diagnostic Systems GmbH AOS 4.1 µcron 62. Before the measurement, the instrument was calibrated to the spectrum of neon. The emitted photons from the plasma were collected by an optical fiber to AES and sent to the spectrometer via a viewport in the chamber. Because of photon absorption by the viewport at wavelengths shorter than 400 nm, the scanning range was set to 400–800 nm and a 1-nm step size was used. The collection time for each step was 0.01 s and the voltage to the photo multiplier tube was set to 1000 V.

Ultraviolet-visible spectrophotometer (Shimadzu, UV-2450) was used for OES measuring the band gaps of the films grown on sapphire substrates. It should be noted that Si has a smaller band gap (1.1 eV) than Ta₂O₅Nₓ-Oₓ (~ 2.1 eV) and can absorb photon energy larger than band gap, which is not the proper substrate used for this OES measurement. Herein, the sapphire was used as the substrates and the absorption spectrum of sapphire was measured as background. The spectra were collected in the range of 250–900 nm. The band gaps for the samples were calculated utilizing the Tauc method.
3. Results and discussion

3.1. Structure and chemical composition of as-grown films

3.1.1. Crystalline structure

The crystalline structure of as-grown films was characterized by X-ray diffraction (XRD) and are shown in Fig. 1. From films deposited without introducing oxygen in the reactive gas, the diffractogram showed one high intensity peak located at \(2\theta = 35.89\), and one low intensity peak at \(2\theta = 41.67\), corresponding to the 111 and 200 diffraction peaks of cubic \(\delta\)-Ta\(N\) according to the inorganic crystal structure database (ICSD) pattern no.07-6456, in addition to the 111 and 222 Si substrate peaks at \(2\theta = 28.56\) and 58.86°, see Fig. 1(a). Below the measurement, the diffraction histogram for cubic \(\delta\)-Ta\(N\) is shown, and the diffraction pattern indicates that the sample was grown preferentially along 111 orientation. When introducing –2% of \(O_2\) into the gas mixture of \(Ar\) and \(N_2\) during growth, the XRD measurement for the sample grown at 5 mTorr total pressure shows very different patterns to \(\delta\)-Ta\(N\). Multiple diffraction peaks located at \(2\theta = 17.35, 31.45, 35.02, 36.04, 39.33,\) and 53.82° were measured, as shown in Fig. 1(b), revealing a polycrystalline structure. These peaks correspond to \(\{020\}/\{002\}\), \(\{023\}\), \(\{113\}\), \(\{042\}/\{004\}\), \(\{200\}\), and \(\{060\}/\{006\}\) planes of orthorhombic Ta\(3N_5\) films, respectively, plotted according to ICSD pattern no.06-6533. The orthorhombic Ta\(3N_5\) structure belongs to the space group of \(I\overline{4}2m\). Since the difference between \(b\) and \(c\) lattice constants is only ~0.05 Å, the family of XRD peaks \((0k0)\) and \((00l)\), where \(k \neq l\), become difficult to distinguish and are presented in the form of \((00l)/(00l)\) in this study. The above results show that the \(O_2\) and \(N_2\) are important gases to trigger the formation of orthorhombic Ta\(3N_5\) phase.

The effect of total working pressure on the crystalline structure was studied by changing the total pressure from 5 to 40 mTorr while keeping the same partial pressure ratio \((N_2:Ar:O_2 = 3:2:0.1)\). Fig. 1(c) shows that the Ta\(3N_5\) phase remains, and a transition from polycrystalline to a fiber-texture-like structure with prefer orientation dominated by \((00l)/(00l)\) occurs with increasing pressure from 5 to 30 mTorr. At a further increase in working pressure up to 40 mTorr, the film becomes amorphous. In addition, the peaks of \((00l)/(00l)\) of Ta\(3N_5\) films slightly shift to higher diffraction angles when the total working pressure increases from 5 to 30 mTorr indicating a decreasing interplanar spacing. Due to the orthorhombic structure, the \(a\), \(b\), and \(c\) lattice constants can easily be obtained from \(d_{hlk}\) spacing of \((00l), (00l),\) and \((00l)\) with formulas of \(h \cdot d_{00l} = k \cdot d_{0l0} + l \cdot d_{00l}\), respectively. The \(b\) - or \(c\)-lattice constant of the Ta\(3N_5\) crystal versus working pressure is plotted in Fig. 1(d), which shows a clear decrease in lattice constant with increasing pressure, and the largest lattice constant difference between 5- and 30-mTorr samples is 0.13 Å (~1.3% of \(b\) or \(c\) lattice constant).

3.1.2. Chemical bonding

The films were further characterized by XPS to study the bonding structure. Fig. 2(a) and (b) show sets of XPS Ta 4f and N 1s core-level spectra, respectively, from Ta\(N\), 5, 30, and 40 mTorr samples. To avoid destructive effects of the \(Ar^+\) ion etch, the results shown in Fig. 2 (a) and (b) were obtained directly from as-grown films without surface sputtering.

Fig. 2(a) shows that all Ta 4f spectra consist of two main peaks, which are attributed to \(4f_{7/2}\) and \(4f_{5/2}\) spin-split components. For the sample grown without oxygen, \(N_2:Ar = 3:2\), the two Ta 4f peaks are located at 23.6 and 25.5 eV, see the bottom most spectra in Fig. 2(a), indicating formation of \(\delta\)-phase Ta\(N\) [33-36]. This is further confirmed by the position of the peaks. The black guiding lines are diffraction peaks of 5 mTorr sample. (d) The corresponding \(b\) or \(c\)-lattice constant versus the total working pressure of the samples grown from 5 to 30 mTorr. The lattice constant is calculated from the \((020)/(002)\).
by the relatively high binding energy of the corresponding N 1s peak, 397.8 eV, see the bottom most spectrum in Fig. 2(b), as well as XRD results, see Fig. 1(a). A small shoulder visible on the high binding energy side of the Ta 4f5/2 peak at around 27.8 eV is assigned to the residual Ta–O [29]. For samples grown at 5 mTorr gas mixture with ~2% of oxygen, N2:Ar:O2 = 3:2:0.1, the Ta 4f peaks shift towards higher binding energies with 4f7/2 and 4f5/2 peaks at 26.7 and 24.8 eV, respectively, while the corresponding N 1s peak moves in the opposite direction to 396.7 eV, indicating Ta3N5 formation [6,34–40]. Observed binding energy (BE) shifts reveal an increased charge transfer between Ta and N atoms (with respect to the δ-TaN), which likely results from the higher N coordination number and shorter Ta–N bond length [41]. Sample deposited at 30 mTorr shows essentially the same result. These spectra confirm the formation of Ta3N5-type Ta-N-O compound. However, in the case of the 40-mTorr sample, the Ta 4f spectrum shows evidence for the Ta-oxide formation, as the peaks move to higher BE and become broader, which is characteristic of phase mixture. Spectra deconvolution suggests the presence of monolithic TaON phase (Ta 4f7/2: 25.8 eV, Ta 4f5/2: 27.7 eV [6,36]) and Ta2O5 phase (Ta 4f7/2: 26.6 eV, Ta 4f5/2: 28.5 eV [42]). Evidence for residual amount of Ta2O5 is also evident in the 30 mTorr spectra. Evidence for residual amount of Ta2O5 is also evident in the 30 mTorr spectra.

Fig. 2. (a) Ta 4f and (b) N 1s and Ta 2p core level X-ray photoelectron spectroscopy (XPS) spectra of TaN sample (without oxygen), 5, 30, and 40 mTorr samples (~2% oxygen in gas mixture for all working pressures).

Fig. 3. Analysis of chemical composition determined by elastic recoil detection analysis (ERDA). Elemental depth profiles obtained by (a) 8-TaN sample, (b) 5-mTorr, and (c) 40-mTorr samples. (d) Total working pressure versus atomic fraction, Ta, N, and O, of samples deposited at 5, 10, 15, 20, 30, and 40 mTorr (keeping ~2% of O2 in gas mixture for all working pressures). The value is the average between 50–1015 atoms/cm2 and 500–1015 atoms/cm2. Note: the Ta, N, and O atomic fractions are summed up to 1. The dash lines label the fraction of pure Ta3N5.
mTorr sample.

3.1.3. Chemical composition

To study the stoichiometry of as-grown samples, ERDA is used to quantify the chemical composition. Fig. 3(a), (b), and (c) are three representative depth profiles measured from the TaN, 5 and 40 mTorr samples to show oxygen-free, low- and high-incorporation of oxygen films, respectively. Apart from information on the atomic fraction of elements in the films, the depth profiles allow also to obtain thickness information if density of the films is known. From Si profiles, a trend of thickness variation gives a result of sample 5 mTorr: 40 mTorr > 6-TaN, which also refers to the same correspondence in deposition rate at a fixed deposition time. The result of thickness trend is in agreement with the thickness measured from scanning electron microscopy (not shown here), which the thickness of 5 mTorr, 40 mTorr and 6-TaN is around 124, 101, and 56 nm, respectively.

Fig. 3(a) shows an ERDA depth profile of the 6-TaN film grown in a gas mixture with only Ar and N2. The Ta and N profiles show the same trend oppositely to Si throughout the entire regime. Although the signal of Si is seen from the beginning of the depth profile due to the small thickness of the film makes energy loss straggling of more heavy species problematic and smears out the energy profile, the N/Ta ratio is not expected to be significantly affected, as long as the profiles of these two are proportional to each other. The atomic fraction of Ta and N in the film are 0.324 and 0.546, respectively, which yields a N/Ta ratio around 1.67, indicating an over-stoichiometry from excess N. The high N/Ta ratio is in fact equivalent to the stoichiometry of Ta3N5 phase. The signal 1.67, indicating an over-stoichiometry from excess N.

The high N/Ta ratio is over 3. The result indicates a high possibility of phase transition from TaN5 type structure to a mixing phase with TaON and Ta2O5 as the results, as obtained from XPS measurement, implying that O takes main role in reaction with Ta to form a new phase. Hence, the film dominated by Ta-oxide compounds is referred to as amorphous O-rich TaNxOy.

3.1.4. Discussions on structural properties of as-grown films

The results of XRD, XPS, and ERDA, summarized in Table 1, show that the crystalline structure and chemical composition of Ta-N-O compound films are highly sensitive to the growth conditions. Oxygen is found to be a decisive role to alter forming the crystalline structures of the sputtered films from β-TaN to orthorhombic TaN5-type TaN5, TaON or amorphous O-rich TaNxOy compounds when the process gas was added with a small of oxygen and increased with working pressure.

By adding ~2% of oxygen in the process gas, the crystalline TaN5-type structure was formed and stabilized. We also made attempts to grow TaN5 without oxygen assistance by varying growth conditions, such as temperature, the partial pressure ratio of N to Ar, magnetron power, and the use of substrate. However, only metallic TaN compounds, including β-TaN, n-TaN, and other TaN5 (x < 1) films, were formed in our deposits (not shown here), which is in agreement with a previous report [22] for the difficulty in growing TaN5 films. The effect of oxygen, which increases the stability of a compound with high-oxidation-state transition metal atoms by replacing its bonding partner with an atom having a higher electronegativity, called inductive effect [23], triggers the formation of crystalline TaN5-type structure. In addition, the oxygen is seen into the growth, but not only acts as a role of catalyst, as seen in the results of XPS and ERDA.

The stability of metastable TaN5 structure was studied by modelling structure from a 96-atom orthorhombic TaN5 supercell using density-functional theory (DFT), reported by Harb et al. [7]. Their calculation showed much enhancement in structural stability by partial replacement of nitrogen with oxygen in the model, which five neutral N atoms at specific sites having two N4, two N5 and one N3 sites [43] were replaced by five O atoms, on b planes. Such a replacement results in the change of b lattice constant more than a and c lattice constant and generation of one Ta vacancy. The chemical formula of the compound was hence referred to as TaN5.5O0.5. The incorporated oxygen atoms in the crystal were mainly contributed to the substitutional and unavoidable. In addition, the formation energy of intrinsic defects using spin-polarized DFT calculation reported by Jing et al. also shows that the substitution of O for N is the most stable among all of defects in TaN5 [44]. The results in their modelling are consistent with our ERDA result that the trend of O and N varied oppositely with working pressure shown in Fig. 3(d). Assuming all incorporated O atoms substitute N sites, then

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Summarized results of XRD, XPS, and ERDA.</th>
</tr>
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<tbody>
<tr>
<td>Sample</td>
<td>XRD Crystalline structure</td>
</tr>
<tr>
<td></td>
<td>Lattice constant (Å)</td>
</tr>
<tr>
<td>TaN</td>
<td>β-TaN</td>
</tr>
<tr>
<td>5 mTorr</td>
<td>TaN5</td>
</tr>
<tr>
<td>10 mTorr</td>
<td>TaN5</td>
</tr>
<tr>
<td>15 mTorr</td>
<td>TaN5</td>
</tr>
<tr>
<td>20 mTorr</td>
<td>TaN5</td>
</tr>
<tr>
<td>30 mTorr</td>
<td>TaN5</td>
</tr>
<tr>
<td>40 mTorr</td>
<td>Amorphous</td>
</tr>
</tbody>
</table>

* Sample-TaN a lattice constant of 6-TaN. Samples with TaN5-type structure: a or c lattice constant.
ratio of non-metal to metal, (N + O)/Ta, of stoichiometric Ta2N3O8 films should be kept at 1.67. However, an over stoichiometry of excess non-metal elements of the as-grown films was always obtained from ERDA, see Table 1. By calculating the elemental ratio according to Harb’s assumption of chemical formula Ta3N5−5xO5x using O atomic fraction obtained from ERDA as the base, we find that over stoichiometry of these films is mainly associated with excess N and deficiency of Ta atoms, which may result in the generation of N interstitials and Ta vacancies, in the pressure region of 5–30 mTorr. Other defects, such as O and Ta interstitials and N vacancies, with higher formation energy cannot be completely excluded since they may be generated by energetic reactive species in magnetron sputtering process. Among them, O interstitials have high possibility to be increased with pressure as the non-metal atomic fraction does not change too much. However, contribution of other defects in determining the non-metal to metal ratio is relatively low. The N becomes deficiency, and the over stoichiometry of non-metal elements is even higher in 40-mTorr sample, (N + O)/Ta = 3.03, if the structure model is used in other Ta3N5-type phases. This transition indicates that the constitution of the film becomes oxide dominant rather than nitride, which matches the present XPS result that the film contains Ta2O5 and TaON compounds. In addition, previous study shows that the formation of crystalline O-rich Ta2ON film requires annealing temperature higher than 900 °C [11]. Hence, the O-rich Ta2ON film grown at 800 °C is thought too low to form crystalline.

The confirmation of forming Ta2N3O8 compound alloys with varied atomic fraction further explains the decrement of b and c lattice constant of the films grown with increasing working pressure from 5 to 30 mTorr, see Fig. 4(d) and Table 1. For 5-mTorr sample, the obtained lattice constant is 10.30 Å, which is larger than the b lattice constant of Ta2N5 crystal, 10.21 Å, shown in ICSD database. (It should be noted that the O content was not specified in the database.) As the O atomic fraction is as low 0.022, this deviation in lattice constant is mainly associated with the formation of excess interstitial N atoms, which contributes isotropic tensile strain component to the film, as seen in other nitride films with over stoichiometry of N [46]. With increasing atomic fraction of O, the b or c lattice constant of Ta2N5O8 compounds becomes smaller. The shortest lattice constant obtained from the 30-mTorr sample is 10.17 Å, which has an around 1.3% decrement (0.13 Å) compared to 5-mTorr sample. Similar result was also obtained from calculated lattice constant of Ta2N5O8 compounds using DFT method by Harb et al. The decrement of b and c lattice constants decrease monotonically with increasing O incorporation.

3.2. Reactive species

Because the partial pressure ratio of O2 in the gas mixture was fixed at ~2% (N2:Ar:O2 = 3:2:0.1), the result that increase of incorporated O in the films with total pressure is noteworthy. Therefore, the in-situ OES technique was used to characterize the plasma during the sputtering in a total working pressure range of 5–40 mTorr. Fig. 5(a) shows the emission spectra of the plasma generated by ~40 mTorr in gas mixture of Ar + N2 (top) and Ar + N2 + O2 (bottom). The spectra can be divided into three dominant regions: i) Three sharp-emission peaks from Ta located at 534, 539, and 581 nm [47]; ii) fingerprint envelope from molecular nitrogen emission in 620–690 nm; and iii) fingerprint envelope from atomic nitrogen emission in 710–780 nm. Since the emission from oxygen transitions overlaps (777.4 nm) [48], with nitrogen transitions, the difference in intensity of the fingerprint envelopes should be observed when the ratio of oxygen partial pressure changes. By comparing these two spectra, no obvious difference is seen in the region of nitrogen dominated emissions, indicating that the oxygen partial pressure ratio is still very low. However, the intensity of Ta transition peaks drops drastically in the gas mixture with oxygen, implying that the sputtering yield of Ta decreases.

Fig. 5(b) shows the dependence of intensity’s difference of Ta transitions before and after O injection plotted as a function of total working pressure. Deviation of Ta transition’s intensity becomes larger as increasing working pressure, indicating a higher reduction in Ta sputtering yield. The lower sputtering yield is expected to have a lower growth rate. From ERDA measurement, the lower growth rate is confirmed as the thickness of 40-mTorr sample is indeed less than 5-mTorr sample, see Fig. 3(b) and (c). The results shown above imply that O has higher reactivity to Ta in comparison to N, which is in line with the fact that metal has higher affinity to oxygen than nitrogen and a more negative enthalpy of formation of tantalum pentaoxide (−488.8 kcal/mol) in comparison to tantalum nitride (−60.0 kcal/mol) at 25 °C [49,50]. Although the partial pressure ratio of O2 in the process gas is kept as ~2%, total amount of O2 still increases with increasing total working pressure. More oxides can be formed on the top of Ta target, which results in a higher degree of target poisoning. The sputtering yield of an oxide layer on Ta target is less than pure Ta target, but reactive species contain higher O, which leads to a higher amount of O incorporated into the deposited film. The OES result hence explains the peculiarity that the O atomic fraction in the films increases noteworthy from 0.022 to 0.486 with total pressure varying from 5 to 40 mTorr at a kept ~−2% O2 in the processing gas mixture, N2:Ar:O2 = 3:2:0.1.

3.3. Optical properties

The effect of incorporated O in the films on the optical property of Ta2O-N samples was determined by OAS at room temperature. Tauc’s method was used to determine band tails and the optical bandgaps from the optical absorption spectra of the samples. The plot is based on Tauc’s equation (\(A\nu^2 = B(\nu - \nu_E)\)) and \(n = \frac{1}{h}\) is used for indirect bandgap materials [51], where A is the absorption coefficient, \(B\) is a constant, \(\nu\) is the angular frequency of incident radiation, \(h\) is Planck’s constant, and \(\nu_E\) is the bandgap. \(\nu_E\) can be extracted from the curve of \((A\nu)^2\) plotted as a function of \(\nu\) (incident photon energy) by extrapolating a tangent line intersected with photon energy axis. Fig. 5(a) shows Tauc plots of the films deposited on sapphire substrate in a working pressure range of 5–40 mTorr. (Note, chemical compositions of these films are the same as the films grown on Si substrate counterpart, which was confirmed by ERDA measurement.) As can be seen in the spectra, the absorption edge shifts apparently towards higher energy when the samples were grown at higher total working pressure, indicating that the bandgap becomes wider as the atomic fraction of O in the film is increased. The extracted bandgap plotted as a function of O atomic fraction is shown in Fig. 5(b).

The bandgap increases monotonically (slightly linear) from around 2.22 to 2.66 eV with increasing O atomic fraction from 0.022 to 0.148.
correspondently. The smallest bandgap of the Ta3N5O film is very close to the theoretically calculated bandgap of Ta3N5, 2.0 ± 0.2 eV [4-8]. In addition, a tail at the lower energy side of the absorption edge was also seen in many Ta2N5 films prepared by two-step growth [52]. The band tail, which also called as Urbach energy, is often correlated to the degree of structural disorder and point defects as seen in other semiconductors [53]. When the O atomic fraction raises to 0.483 (40-mTorr sample), the optical bandgap increases to around 2.96 eV. Such a change is reasonable because the crystalline structure and chemical composition of the film have changed to an O-rich TaNxOy compound, mixed with TaON and Ta2O5. The absorption is, therefore, more approached to the calculated bandgap of TaON, ~3 eV [7].

According to the calculated electronic density of state (DOS) using DFT methods [7], the valence band of pure TaN5 is mainly governed by the s orbitals of Ta atoms and the 2p states of N atoms, while the conduction band is composed of the d orbitals of Ta atoms, which is mainly responsible for the intrinsic n-type conduction of TaN5 [44,52]. At lower-level O incorporation, the donors can form localized states below conduction band minimum. With increasing O atomic fraction, more electrons can fill the conduction band, which further broadens the optical band gap. On the other hand, N vacancies was counted to be ~0.02 between 5- and 30-mTorr samples. Meanwhile, the decrement of Ta atomic fraction to 0.148 as increasing total working pressure, while N decreased with a reverse trend to the O counterpart. The decrement of Ta atomic fraction was counted to be ~0.02 between 5- and 30-mTorr samples. Meanwhile,

centered at ~1.72 eV [52]. Although our films always show over stoichiometry with excess N, the formation of N vacancies cannot be ruled out. Other defects, such as N, O interstitials and Ta vacancies in the lattice, mostly cause even deep level bands. As to the O-rich TaN5O compound, the band gap of monoclinic TaON was predicted to be around 3 eV [7].

DOS calculated by DFT shows that O 2p states become dominant in the valence band. With increasing a bit more N atomic fraction, the bandgap is narrowing towards to 2.5 eV owing to more N 2p states located at higher energy of valence band. Optical properties of TaON films, made by high-power impulse magnetron sputtering, studied by variable angle spectroscopic ellipsometry confirmed that the bandgap increases from 2.5 eV towards to 3.9 eV (Ta2O5) with increasing O/N ratio [11]. In summary, our OAS result is in consistency with the DFT calculation that substitution of O atoms for N sites in Ta2N5O3 film plays a decisive role in determining of optical properties.

4. Conclusions

Orthorhombic Ta3N5O3 compound films with various atomic fractions grown directly on Si and sapphire substrates using reactive magnetron sputtering on a Ta target was achieved by adjusting total working pressure in a gas mixture of N2, Ar, and O2 (keeping partial pressure of 3:2:0.1). In the pressure regime of 5-30 mTorr, all films were grown in Ta2N5-type crystal with a low degree of fiber texture along b-axis direction. The atomic fraction of O in the films increased from 0.022 to 0.148 as increasing total working pressure, while N decreased with a reverse trend to the O counterpart. The decrement of Ta atomic fraction was counted to be ~0.02 between 5- and 30-mTorr samples. Meanwhile,
the work reported in this paper. All authors have contributed to the writing and agreed to the published version of the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References


Paper II

Domain epitaxial growth of Ta₃N₅ film on c-plane sapphire substrate

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Surface and Coatings Technology, Volume 443, 15 August 2022, 128581

https://doi.org/10.1016/j.surfcoat.2022.128581

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ARTICLE INFO
Keywords: Ta₃N₅, Sputtering, XPS, MSE, Water splitting. Crystal Ta₃N₅ film with epitaxial domains on single-crystal Al₂O₃(0001) substrates was obtained with the addition of a Ta2O5 seed layer. A single-phase polycrystalline Ta₃N₅ film can be obtained with the assistance of a Ta2O5 seed layer. With controlling thickness of the seed layer smaller than 10 nm and annealing at 1000 °C, a crystalline β-phase Ta2O5 was formed, which promotes the domain epitaxial growth of Ta₃N₅ films on Al2O3(0001). The mechanism behind the stabilization of the orthorhombic Ta₃N₅ structure resides in its stacking with the ultrathin seed layer of orthorhombic β-Ta2O5, which is energetically beneficial and reduces the lattice mismatch with the substrate.

1. Introduction

The semiconductor tritantalum pentanitride (Ta₃N₅) is a potential green-energy material for photoelectrolysis of water to produce oxygen and hydrogen thanks to its proper bandgap of 2.0 ± 0.2 eV [1-4] and band positions to redox potential of water [5,6]. The water splitting efficiency using Ta₃N₅ is predicted to be as high as 15.9% [7,8]. However, Ta₃N₅ is a metastable phase in the complex phase diagram of several binary tantalum nitride (Ta–N) compounds [9,10]. Conventionally, a two-step process of oxidation and nitridation of metal Ta foil using thermal annealing in oxygen and ammonia environments, respectively, is the way to produce high-phase-purity Ta₂O₅ and Ta₃N₅ films [3,11]. Alternatively, direct growth of Ta₂O₅ onto substrates using magnetron sputtering and atomic layer depositions are reported [4,12-14]. However, direct growth of Ta–N films preferentially leads to the formation of stable phases, metallic β-TaN and ε-TaN [9,13,14]. The metastable Ta₂N₅ phase can be stabilized by a small amount of ~2% oxygen added into the reactive gas used in reactive magnetron sputtering. The oxygen gas was confirmed to play a vital role in inducing high-oxidation-state Ta atoms, which have higher electronegativity to trigger the formation of the Ta₂N₅ phase [4,15,16].

Nonetheless, to date, the structure of as-grown Ta₃N₅ films directly onto a substrate (without seed layers) was mostly reported in amorphous or polycrystalline no matter which growth technique was used. Many researches have been devoted to improve the crystalline quality of Ta₃N₅ films; for instance, by increasing the nitridation time and temperature in the two-step process [17,18], using single-crystal substrates [13], enhancing ionization degree in magnetron sputtering process [13,19,20] or post-nitridation treatment to as-grown sputtered films [18]. However, these experiments show limited improvements; the films still contain a large number of grain boundaries, structural defects, and disordered lattices, resulting in the formation of carrier trapping centers, which deteriorates the performance of any potential device and thus impedes applications [17,19,21].

In contrast, single-crystal Ta₃N₅ films that contain less grain boundaries, point defects and dislocations are expected to significantly improve both performance and lifetime of the materials used for water splitting. In addition, as assessed by density functional theory (DFT) calculations employing the screened nonlocal hybrid HSE06 functional, which is well-known for delivering an accurate description for the electronic properties of compounds, Ta₃N₅ slabs of different orientation show different redox features and carrier mobility [22]. The latter study suggests that the (110) and (001) orientations are suitable candidates for O₂ evolution reactions (HER), while the (010) orientation is a suitable candidate for O₂ evolution reactions (OER). As a reason for such behavior, the different coordination number of the exposed species and...
their structural arrangement are pointed out [22]. Moreover, the band gap of different surface orientations varies due to the different number and energetics of dangling bonds on the surface, which also generates surface states near the valence and conduction band maximum (VBM and CBM). [23] However, to date, the lack of success in growing single-crystal TaN$_N$ precludes the experimental study of the mentioned properties. Without systematic studies and understanding of the properties of single-crystal TaN$_N$, in detail, any further control and improvement of the growth recipes of TaN$_N$ are challenging.

Growth of high-quality epitaxial film is often assisted with a seed layer to reduce lattice mismatch between the film and substrate, for example, improving the GaN and InAlN film's quality using isostructural buffer layer [24-25]. Metastable phase epitaxial films can be grown with a guidance from the other material, which has a similar atomic arrangement of substrate/seed (or buffer) layer surface, for instance, metastable cubic GaN film grown on GaAs(001) substrate [26], cubic arrangement of substrate/seed (or buffer) layer, for instance, buffer layer [24,25]. Metastable phase epitaxial films can be grown using a tetragonal NbO$_2$ seed layer [28]. To explore the possibility to grow single-crystal TaN$_N$ films, one can take the strategy of using TaO$_x$ seed layer with its suitable crystal structure, possessing appropriate interfacial energy, as a structural template. Various structures of Ta–N compounds, including metallic TaN$_x$, mixed phase of TaN and TaN$_N$, and polycrystalline TaN$_N$ film were obtained through the introduction of small amounts of oxygen in the reactive gas using magnetron sputtering as some research reported before [4,14,15]. In this work, we demonstrate that a nearly-single-crystal TaN$_N$ film with epitaxial domains can be grown on c-plane sapphire substrates using direct-current magnetron sputter epitaxy (DCMSE) in a gas mixture of Ar, N$_2$, and O$_2$ after introducing a TaO$_x$ seed layer. The role of the oxide seed layer on determining phase and epitaxy of the Ta–N films is discussed in detail. The structure and chemical composition of the film and the seed layer were analyzed by x-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS). Epitaxial relationship between the film and the substrate was determined using x-ray diffractometry and x-ray photoelectron spectroscopy (XPS). The surface chemistry was characterized by XPS analysis using a Kratos Axis Ultra DLD instrument with monochromatic Al K$_\alpha$ radiation (h$_\nu$ = 1486.6 eV). To avoid the destructive effects of Ar$^+$ ion etching, the measurements were conducted on pristine samples. XPS spectra were collected from a 0.3 $\times$ 0.7 mm$^2$ area in the center of the sample with electrons emitted along the surface normal. The spectrometer was calibrated according to ISO standards [31]. The spectra from polycrystalline films grown on Si substrates were referenced to the Fermi edge cut-off [32] to avoid uncertainties associated with using the C 1s peak of adventitious carbon for that purpose [33]. Spectra recorded from films on insulating substrates were aligned against those obtained from polycrystalline films as no Fermi edge is available in this case. The peak shifts resulting from charging observed for the insulating substrate was compensated by using spectra recorded from a polycrystalline film grown on the Si substrate. For high energy resolution scans, the pass energy of the analyzer was set to 20 eV, resulting in the Ag 3d$_{5/2}$ peak with a full width at half maximum of 0.35 eV. The software casaXPS was used for data analysis. The quantification was performed based on peak areas and elemental sensitivity factors from Kratos Analytical Ltd.

The crystal structure and atomic arrangement of orthorhombic TaN$_N$ and $\beta$-TaO$_x$ and rhombohedral $\alpha$-AlO$_x$ were obtained using a ball-and-stick model via the visualization for electronic and structural analysis (VESTA) software. The structural models of the orthorhombic TaN$_N$, orthorhombic $\beta$-TaO$_x$, as well as AlO$_x$, thus; assessing how the ultrathin seed layer of the $\beta$-TaO$_x$ contributes to the stabilization of TaN$_N$.

2. Experiments

2.1. Sample growth

Ta–N compound films were deposited on c-plane sapphire, Al$_2$O$_3$(001), single-crystal substrates in an ultrahigh vacuum (UHV) DC magnetron sputter deposition chamber with a background pressure of 5 $\times$ 10$^{-6}$ Torr. A type-II unbalanced magnetron was used to guide the plasma to substrate [29]. A continuous substrate rotation of 200 rpm was applied to ensure the homogeneity of as-grown films for all depositions. More details can be found elsewhere [15,30]. Prior to the film growth, the substrates were cleaned by acetone and isopropanol sequentially in ultrasonic bath for 5 min each and dried by blowing nitrogen before loading into the chamber. All Ta–N compound films were deposited using a high-purity (99.999%) Ta target sputtered reactively in a gas mixture of N$_2$ (3 mTorr), Ar (2 mTorr), and with or without O$_2$ (0.1 mTorr), –2% in total pressure) at 1000 °C. The magnetron power and deposition time were set to 300 W and 20 min, respectively, yielding an ~100-nm-thick film [15]. As to the growth of seed layers, TaO$_x$ layers were sputter deposited on sapphire substrates at room temperature at different deposition times of 3, 5, to 10 min in the same chamber. The growth rate of the seed layer was estimated to be around 1.7–1.8 nm/min measured by spectroscopic ellipsometry. Afterwards, these seed layers were annealed at 1000 °C for 15 min before Ta–N film growth. The growth condition with main variables of samples is listed in Tables 1 and 2, presented together with results and discussion in Section 3.1 and 3.2, respectively.

2.2. Structural and compositional characterizations

The crystalline structure of the films was characterized by 0-20 XRD measurements using a Philips PW1710 Bragg-Brentano powder diffractometer and Cu-K$_\alpha$ radiation with a wavelength of 0.15406 nm. The X-ray tube voltage and current were set to 40 kV and 40 mA, respectively, and a scanning range of 20 – 15° was used with a step size of 0.03° and time per step of 2 s/step. To further determine the epitaxial relationship between the film and the substrate, azimuthal $\omega$-scans were performed in a grazing-incidence diffraction (GID) geometry using a PANalytical Empyrean X-ray diffractometer with a parabolic mirror as the primary optics and a 0.2° parallel plate collimator as the secondary optics. The scanning range was $\psi$ = 0°–360° with a 1° step size and a 1 s/step scanning time for the film and a 0.2° step size with 0.5 s/step for the substrate.

The surface chemistry was characterized by XPS analysis using a Kratos Axis Ultra DLD instrument with monochromatic Al K$_\alpha$ radiation (h$_\nu$ = 1486.6 eV). To avoid the destructive effects of Ar$^+$ ion etching, the measurements were conducted on pristine samples. XPS spectra were collected from a 0.3 $\times$ 0.7 mm$^2$ area in the center of the sample with electrons emitted along the surface normal. The spectrometer was calibrated according to ISO standards [31]. The spectra from polycrystalline films grown on Si substrates were referenced to the Fermi edge cut-off [32] to avoid uncertainties associated with using the C 1s peak of adventitious carbon for that purpose [33]. Spectra recorded from films on insulating substrates were aligned against those obtained from polycrystalline films as no Fermi edge is available in this case. The peak shifts resulting from charging observed for the insulating substrate was compensated by using spectra recorded from a polycrystalline film grown on the Si substrate. For high energy resolution scans, the pass energy of the analyzer was set to 20 eV, resulting in the Ag 3d$_{5/2}$ peak with a full width at half maximum of 0.35 eV. The software casaXPS was used for data analysis. The quantification was performed based on peak areas and elemental sensitivity factors from Kratos Analytical Ltd.

The crystal structure and atomic arrangement of orthorhombic TaN$_N$ and $\beta$-TaO$_x$ and rhombohedral $\alpha$-AlO$_x$ were obtained using a ball-and-stick model via the visualization for electronic and structural analysis (VESTA) software. The structural models of the orthorhombic TaN$_N$ and $\beta$-TaO$_x$ and rhombohedral $\alpha$-AlO$_x$ were obtained using a ball-and-stick model via the visualization for electronic and structural analysis (VESTA) software. The structural models of the orthorhombic TaN$_N$ and $\beta$-TaO$_x$ were built using lattice constants $a = 3.89$ Å, $b = 10.21$ Å, $c = 10.26$ Å and $a = 6.20$ Å, $b = 3.66$ Å, $c = 3.89$ Å, according to the PDF no. 06-6533 and 04-3498 in the inorganic crystal structure database (ICSD), respectively. The space group used for building the model was CmCm for the TaN$_N$ crystal and Pmmn for the $\beta$-TaO$_x$ crystal.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Seed layer</th>
<th>Film growth</th>
<th>Film thickness (nm)</th>
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<th>XPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>ID</td>
<td>Time (min)</td>
<td>TaN$_N$ (111)</td>
<td>TaN$_N$</td>
<td></td>
</tr>
<tr>
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<td>10</td>
<td>15</td>
<td>0</td>
<td>TaN</td>
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</tr>
</tbody>
</table>

Note: Digi and poly are the abbreviation of domain epitaxy and polycrystalline, respectively.
crystal after modifying by computational simulation [34,35]. The structural model of the \(\alpha\)-Al\(_2\)O\(_3\) substrate was built using the lattice constants \(a = 4.76\ \text{Å},\ c = 12.99\ \text{Å}\), and a \(R-3\overline{1}\) space group according to the Springer Materials database [36].

2.3. Computational details

Geometry optimizations of the crystal structures of orthorhombic Ta\(_3\)N\(_5\), orthorhombic \(\beta\)-Ta\(_2\)O\(_5\), and the substrate \(\alpha\)-Al\(_2\)O\(_3\) were carried out within the framework of DFT in its generalized gradient approximation (GGA) as implemented in Vienna ab initio simulation package (VASP) [37]. Pseudopotentials as per the projector-augmented-wave (PAW) method [38] and the Perdew–Burke–Ernzerhof (PBE) level of theory [39] were employed. A standard plane wave cutoff energy of 500 eV was used. The relaxation of the crystal structures was considered converged when the residual force on each atom reached the criterion of 0.001 eV/Å, while the energy convergence criterion in geometry optimizations was set to 0.001 eV per atom.

3. Results and discussion

3.1. Formation of polycrystalline Ta\(_3\)N\(_5\) film

The effect of different combinations of a small amount of O\(_2\) (~2% in total pressure) added to the sputtering gas and the usage of a thin TaO\(_x\) seed layer on the stabilization of a metastable Ta\(_3\)N\(_5\) phase was studied. The main growth parameters together with summarized XRD and XPS results are listed in Table 1.

The crystalline structure of the films characterized by XRD is shown in Fig. 1. When a Ta–N film was directly deposited on the sapphire substrate without oxygen gas assistance, only two peaks, located at 34.55° and 35.89°, were observed in addition to the Al\(_2\)O\(_3\)(0006) peak located at 41.80°, shown in Fig. 1(a). These two peaks correspond to cubic \(\delta\)-TaN(111) and hexagonal \(\varepsilon\)-TaN(110) according to the PDF no. 07-6456 and no. 00-1396, respectively, indicating a phase-mixed film. With introducing a TaO\(_x\) seed layer, the film only contained the \(\delta\)-TaN phase grown preferentially along the [111] growth orientation on Al\(_2\)O\(_3\)(0001), see Fig. 1(b). The above results agree with previous studies that both \(\delta\)- and \(\varepsilon\)-TaN phases are more thermodynamically stable among others in this complex binary compound system [40]. Using a seed layer allows to form a single-phase epitaxial \(\delta\)-TaN(111) film on Al\(_2\)O\(_3\)(0001).

Since O\(_2\) proved to have a key role in the stabilization of the metastable Ta\(_3\)N\(_5\) phase [14,15], we further studied the growth of Ta–N thin films in a reactive deposition atmosphere containing ~2% O\(_2\). However, instead of Ta\(_3\)N\(_5\), a single-phase \(\delta\)-TaN(111) epitaxial film was formed on Al\(_2\)O\(_3\)(0001) substrates, see Fig. 1(c). After introducing a TaO\(_x\) seed layer, a multiplex XRD pattern was obtained, where the peaks were located at \(2\theta = 17.35°,\ 31.45°,\ 35.02°,\ 36.04°,\ 39.33°\) and 53.82°, Fig. 1(d). According to the PDF no. 06-6533, these peak positions correspond to the 020/002, 023, 040/004, 113, 042/024, and 060/006 planes of Ta\(_3\)N\(_5\).

Table 2

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Deposition time (min)</th>
<th>Thickness (nm)</th>
<th>Annealing time (min)</th>
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<th>XPS</th>
</tr>
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<td>9</td>
<td>No</td>
<td>Amorphous TaO(_x)</td>
<td></td>
</tr>
<tr>
<td>S-A1</td>
<td>5</td>
<td>9</td>
<td>15 min</td>
<td>TaO(_2)(201)</td>
<td>TaO(_2)</td>
</tr>
<tr>
<td>S-A2</td>
<td>10</td>
<td>17</td>
<td>15 min</td>
<td>Amorphous TaO(_2)</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. XRD patterns of Ta–N compound films grown (a) without oxygen and seed layer (Sample TN-1), (b) without oxygen but with seed layer (Sample TN-2), (c) with oxygen but without seed layer (Sample TN-3), and (d) with both oxygen and seed layer (Sample TN-S3). Peaks marked with star in Fig. 1(d) are from Ta\(_3\)N\(_5\) phase according to ICSD patterns no. 06-6533. The marked letter S in figures represents the peaks from sapphire’s c planes.
polycrystalline Ta$_3$N$_5$. It should be noted that since the difference between $b$ and $c$ lattice constants is only 0.05 Å and the angular resolution is not sufficient to distinguish between $(0k0)$ and $(00l)$ reflections, when $k = l$. The chemical composition and bonding nature of Ta–N compound films grown without and with the seed layer, i.e., samples TN-3 and TN-S3, respectively, were further characterized by XPS. Both films were all grown with adding ~2% O$_2$ into the sputtering gas. Spectra shown in the left panel of the Fig. 2 reveal only two distinct peaks. Detailed analysis reveals, however, that two sets of 4f$_7/2$/4f$_5/2$ spin-split doublets are necessary for satisfactory fit quality. Two main peaks at 25.2/27.1 eV confirm the formation of Ta$_3$N$_5$ phase [46]. The second doublet with two additional peaks at around 532.0, and 533.0 eV can be assigned to C–O and C=O species that are present in the adventitious carbon accumulating at the surface of all samples [32]. Quantification based on the areas of component peaks gives the Ta:O:N ratio in the oxynitride of 1: 1.5: 0.6.

Fig. 2(a) shows the Ta 4f, N 1s, and O 1s spectra of the thin film deposited directly on a sapphire substrate. The left panel of the Fig. 2(a), the Ta 4f core level spectrum was deconvoluted using Gaussian-Lorentzian (Voigt) peak shape and Shirley-type background. The peak area ratio reveals, however, that two sets of 4f$_7/2$/4f$_5/2$ spin-split doublets are necessary for satisfactory fit quality. Two main peaks at 25.2/27.1 eV confirm the formation of Ta$_3$N$_5$ phase [46]. The second doublet with two additional peaks at around 532.0, and 533.0 eV can be assigned to C–O and C=O species that are present in the adventitious carbon accumulating at the surface of all samples [32]. Quantification based on the areas of component peaks gives the Ta:O:N ratio in the oxynitride of 1: 1.5: 0.6.

The same functions were used during deconvolution as for the N 1s spectra. The main peak located at 393.5 eV corresponds to the oxygen atoms in TaO$_x$Ny that forms on the surface of the film [34,45]. The two additional peaks at around 532.0, and 533.0 eV can be assigned to C–O and C=O species that are present in the adventitious carbon accumulating at the surface of all samples [32]. Quantification based on the areas of component peaks gives the Ta:O:N ratio in the oxynitride of 1: 1.5: 0.6.

Fig. 2(b) shows the Ta 4f, N 1s, and O 1s spectra of the film deposited with a 17-nm seed layer. The Ta 4f spectrum shown in the left panel of the Fig. 2(b) reveals only two distinct peaks. Detailed analysis reveals, however, that two sets of 4f$_7/2$/4f$_5/2$ spin-split doublets are necessary for satisfactory fit quality. Two main peaks at 25.2/27.1 eV confirm the formation of Ta$_3$N$_5$ phase [46]. The second doublet with two additional peaks at around 532.0, and 533.0 eV can be assigned to C–O and C=O species that are present in the adventitious carbon accumulating at the surface of all samples [32]. Quantification based on the areas of component peaks gives the Ta:O:N ratio in the oxynitride of 1: 1.5: 0.6.

The chemical composition and bonding nature of Ta–N compound films grown without and with the seed layer, i.e., samples TN-3 and TN-S3, respectively, were further characterized by XPS. Both films were all grown with adding ~2% O$_2$ into the sputtering gas. Spectra shown in the left panel of the Fig. 2 reveal only two distinct peaks. Detailed analysis reveals, however, that two sets of 4f$_7/2$/4f$_5/2$ spin-split doublets are necessary for satisfactory fit quality. Two main peaks at 25.2/27.1 eV confirm the formation of Ta$_3$N$_5$ phase [46]. The second doublet with two additional peaks at around 532.0, and 533.0 eV can be assigned to C–O and C=O species that are present in the adventitious carbon accumulating at the surface of all samples [32]. Quantification based on the areas of component peaks gives the Ta:O:N ratio in the oxynitride of 1: 1.5: 0.6.

Fig. 2. Ta 4f, N 1s, and O 1s core-level XPS spectra of Ta–N compound films grown (a) without and (b) with a TaO seed layer. The seed layer's thickness of sample is 17 nm. Blue, yellow, and brown lines represent Ta$_3$N$_5$, TaO$_x$Ny, and 6-TaN$_x$ phases, respectively, fitted by Casa XPS software. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
sample, consistent with the higher resistance to oxidation of the Ta$_3$N$_5$ sample. These results confirm that both adding ~2% O$_2$ to the reactive sputtering gas and using a TaO$_x$ seed layer are necessary to trigger the formation of the Ta$_3$N$_5$ phase.

3.2. Growth of Ta$_3$N$_5$ epitaxial domains on sapphire substrate

In heteroepitaxy, a proper seed layer (or buffer layer) is commonly used to promote heteroepitaxial growth, reduce structural defects, and prevent phase separation of the subsequent grown film by decreasing the lattice and thermal-expansion-coefficient mismatches between films and substrates that results in a decrease in lattice distortions and residual strain [24,47,48]. Moreover, the film quality is often determined by the quality and thickness of the used seed layer; for instance, insufficient surface coverage in the island growth mode or defect generation after strain relaxation in the layer-by-layer growth mode.

To study the effect of the TaO$_x$ seed layer thickness on the formation of crystalline Ta$_3$N$_5$ phase, the Ta–N films were grown using the same growth conditions as sample TN-3. The seed layers were grown for 3, 5, and 10 min, with estimated thicknesses of around 5, 9, and 17 nm, respectively. Peaks marked with star in Fig. 1(d) are from Ta$_3$N$_5$ and the Ta$_3$N$_5$ phase, the Ta$_3$N$_5$ phase directly deposited on sapphire. The coexistence of two phases ascribes the formation of polycrystalline Ta$_3$N$_5$, see Fig. 3 that shows the XRD pattern of TN-S3 deposited on a seed layer with a thickness of 17 nm. These results confirm that both adding ~2% O$_2$ to the reactive sputtering gas and using a TaO$_x$ seed layer are necessary to trigger the formation of the Ta$_3$N$_5$ phase.

The crystal orientation of the film grown on the 9-nm-thick seed layer was further studied by acquiring azimuthal θ-scans in a grazing-incidence diffraction (GID) geometry, where the sample holder is tilted to have the sample surface almost parallel to the scattering plane (a sample tilt angle $\theta$ ~90°). In this way, crystal planes perpendicular to the substrate surface can be detected through rotating the azimuthal angle $\varphi$ at a fixed diffraction angle $2\theta$ corresponding to either the film or the substrate. GID θ-scans measured at $2\theta = 46.71°$ and 68.21°, corresponding to Ta$_3$N$_5$(200) and Al$_2$O$_3$(1010), are shown in the upper and bottom panels of Fig. 4(a), respectively. Both the film and the substrate have six peaks obtained at the same $\varphi$-angles with a peak separation of 60°. Similar results were also obtained when using $2\theta = 17.35°$ and 37.78°, corresponding to Ta$_3$N$_5$(020) or (004), and Al$_2$O$_3$(1120), shown in the middle and bottom panels of Fig. 4(b), respectively. We further measured Ta$_3$N$_5$(040) or (004), appeared at $2\theta = 35.12°$, and eighteen peaks are observed in the X-ray scan, see the upper panel of Fig. 4(b). Among them, the $\varphi$-angle of six peaks is well aligned with the $\varphi$-angle of six peaks from Al$_2$O$_3$(1120). The other twelve peaks can be divided into two groups, marked with symbols “x” and “+”, and there is also a separation of 60° between peaks in their own groups. Using one of the Ta$_3$N$_5$(040)’s...
and thus the diffraction peaks labelled \( a \) in yellow, green, blue, respectively. (b) An orthorhombic crystal with planes of \( \{100\} \) or \( \{00k\} \), of the Ta3N5 film measured from normal 0-20 scans are then referred to \( c \) planes, \( \langle 00k \rangle \).

In Fig. 5 (a), an \( \alpha-Al_{2}O_{3} \) viewed as a hexagonal crystal along \( c \)-axis direction, \( \langle 001 \rangle \) was illustrated. It is not surprising to observe a six-fold rotational symmetry from either \( a \) planes - \( \{11\overline{2}0\} \) or \( m \) planes - \( \{10\overline{1}0\} \) of a c-plane oriented sapphire substrate when azimuthally rotating the sample 360° in a θ-scan in GID geometry. However, for the Ta3N5 with an orthorhombic structure, see Fig. 5(b), it is expected to see only two peaks in a 360° θ-scan from either \( a \) planes - \( \{100\} \) or \( b \) planes -\( \{010\} \) of a \( c \)-oriented film, owing to its two-fold rotational symmetry. Therefore, the Ta3N5 film must contain three differently oriented domains, grown epitaxially on the sapphire substrate with \( a \) and \( b \) planes of Ta3N5 parallel to \( m \) and \( a \) planes of \( Al_{2}O_{3} \), respectively, as illustrated in Fig. 5 (c). The domain epitaxial relationship is then concluded as Ta3N5(001)//Al2O3(0001), Ta3N5(100)//Al2O3(1010), Ta3N5(130)//Al2O3(130).

3.3. Structure of the seed layer

The results presented above clearly demonstrate that the seed layer not only stabilizes the formation of metastable Ta3N5 phase, but it also affects the growth behaviour on single-crystal sapphire substrate. The structure and composition of bare seed layers were characterized by XPS and XRD. The seed layers’ growth condition with main variables and summarized results of XPS and XRD are listed in Table 2. To minimize the effect of the oxygen absorption on the surface and further oxidation resulting in possible phase transition when the as-grown films residing for a too long time in atmospheric ambient, the as-grown films were transferred to XPS chamber immediately after deposition.

The XPS spectra of Ta 4f, N 1s, and O 1s, of the films grown at room temperature with and without thermal annealing at 1000 °C, are shown in Fig. 6(a), (b), and (c). No big variation, except for small peak shift within 0.2 eV, can be seen in these spectra. The Ta 4f orbital shows two main peaks located at 26.6 and 28.7 eV, see Fig. 6(a), which well correspond to the 4f7/2/4f5/2 spin-split components of Ta2O5 at 26.6/28.5 eV [49,50]. In Fig. 6(b), the XPS spectra neighbour the N 1s orbital show only one peak located at 405.3 eV, recognized as Ta 4p1/2, while no N 1s peak at around 397 eV, marked with a dash, can be detected. The absence of the N 1s signal implies that the films are composed of pure Ta2O5. The O 1s orbital spectra shown in Fig. 6(c) reveal only one peak located at around 531.1 eV, which matches well to the O 1s orbital of Ta2O5 [50]. The seed layer composition is quantitatively calculated using relative sensitivity factors (R.S.F) of Ta and O are 3.08 and 0.78, respectively, from the database of Casa XPS software. With the R.S.F, the ratio of peak area of O to Ta is calculated to be around 2.39, which is close to the stoichiometric value of 2.5. Therefore, annealing does not lead to a significant change in the chemical composition of the seed layer, in the XPS detection limit.

Although the XPS results show that the seed layers are composed of a pure oxide, the oxygen absorbed on the surface may oxidize sample surface and change the stoichiometry, even for the sample exposed to air for a short time. This can result in a wrong interpretation about the chemical composition of the layers. Here, we exclude those possibilities which can lead to pure oxide formed after samples exposed to air. According to our previous study [15], the surface absorbed oxygen does not fully substitute N in nitride films, including TaN, Ta3N5, and TaOxNy, and cannot transform these phases into pure oxide since the N signals were still detectable from those nitride films even though they had been stored in air for couple of months. The other possibility of forming pure oxide owing to oxidation is when a thin Ta layer was grown instead of nitride or oxide layers. However, we can also rule out this possibility since Ta containing film was obtained only when sputtering using pure Ar, but not the condition used for the seed layer growth in this study.

Fig.7 shows the effect of in situ post-annealing at 1000 °C for 15 min on the XRD patterns of the seed layers. The XRD 2θ-2θ scan of the 9-nm thick seed layer grown at room temperature, sample S-1, has only one peak coming from the sapphire substrate, \( \langle 0006 \rangle \) appeared at 2θ = 41.80°. The result indicates that the layer was formed in an amorphous or disordered nanocrystalline (with nanocrystal size smaller than 2 nm).
structure, i.e., an x-ray amorphous structure. However, in-situ post-annealing the 9-nm-thick seed layer (the layer was immediately annealed in the same deposition chamber after the room-temperature growth), sample S-A1, results in appearing a sharp peak at $2\theta = 37.09^\circ$ that corresponds to the (201) of orthorhombic $\beta$-Ta$_2$O$_5$ according to the PDF no. 04-3498. In addition, no obvious degradation in crystallinity occurred when the sample was stored in air after several weeks, revealing a good structural stability. Opposite to the 9-nm-thick seed layer, the XRD pattern of the in-situ post-annealed 17-nm-thick seed layer, sample S-A2, does not have any obvious peak, revealing that this layer has an x-ray amorphous structure, similar to sample S-1. Thus, the lack of lattice coherence between the film and the 17-nm-thick oxide seed layer or the disordered nanocrystalline oxide layer results in the formation of the polycrystalline Ta$_3$N$_5$ film, as shown in Section 3.2.

### 3.4. Mechanisms for the metastable phase stabilization and epitaxial growth

A ball-and-stick model of crystal structures, created by the VESTA software, was used to visualize the atomic arrangement of crystalline structures and possible epitaxial relationships corresponding to the observations made using XRD and GID. The structure of Ta$_2$N$_5$, $\beta$-Ta$_2$O$_5$, and $\alpha$-Al$_2$O$_3$ terminated with corresponding planes of 001, 201, and 0001 are shown in Fig. 8(a) and (b), and (c), respectively. The atomic arrangement of both Ta$_2$N$_5$(001) and $\beta$-Ta$_2$O$_5$(201) unit cells contains three Ta atoms coordinated with 6 N and O atoms, respectively, and shows similar face-centered-cubic structure. With arranging in-plane orientation of the Ta$_2$N$_5$(001) stacked on $\beta$-Ta$_2$O$_5$(201), we can assume that the most favorable in-plane relationship is Ta$_3$N$_5$[010]//Ta$_2$O$_5$[102] since the lattice mismatch is as small as 2.6%. As to the relationship between $\beta$-Ta$_2$O$_5$(201) and Al$_2$O$_3$(0001), the atomic arrangement of Al$_2$O$_3$(0001) shown in Fig. 8(c) reveals a consequence that the Al–Al distance along the [11\_20] is close to the half of the Ta–Ta distance of $\beta$-Ta$_2$O$_5$ along [102] with only a small mismatch ~4.5%. The small lattice constant mismatch and similarity in atomic arrangement between film, seed layer and substrate therefore depict the condition for epitaxy of Ta$_3$N$_5$ on Al$_2$O$_3$. However, the stacking of orthorhombic on hexagonal crystal results in three possible local epitaxial domains, as shown in Fig. 5.

By carrying out DFT calculations, the relaxed structures of crystalline Ta$_2$N$_5$ (orthorhombic), crystalline $\beta$ phase Ta$_2$O$_5$ (orthorhombic), and $\alpha$-Al$_2$O$_3$ were obtained. The simulation results confirm the small, and perceived as favorable for epitaxial growth, in-plane lattice mismatches for Ta$_3$N$_5$[010]//Ta$_2$O$_5$[102] and Ta$_2$O$_5$(201)/Al$_2$O$_3$(0001), respectively (c.f., Fig. 8). The in-plane lattice mismatches as assessed by the simulation results are 2.4% and 4.3%, respectively, nearly coincide with the corresponding experimental lattice mismatches (~2.6% and ~4.5%). We obtain the formation energies of ~1.25 eV/at, ~3.22 eV/at, and ~3.39 eV/at for Ta$_2$N$_5$ [51], Ta$_2$O$_5$, and Al$_2$O$_3$ [5], respectively, which compare reasonably well to results obtained previously by others for the same quantities and compounds. The difference in formation energies between two possible competitive phases (in the present case, Ta$_2$N$_5$ and Ta$_2$O$_5$) to be grown on the same substrate (Al$_2$O$_3$) can be also seen as one of the factors regulating the competitive selection of compounds during epitaxial growth [52]. Thus, in an epitaxial growth situation, the calculated differences in the formation energies between...

![Fig. 6. XPS spectra of as-grown and annealed TaO$_x$ samples. (a) Ta 4f, (b) N 1s, and (c) O 1s core level spectra. The dash lines marked in (a) correspond to binding energy of Ta$_2$O$_5$ phase. Black and red curves represent as-grown and annealed samples, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image)

![Fig. 7. XRD patterns measured from Ta$_2$O$_5$ seed-layer samples. S-1: 9 nm thickness but without annealing, S-A1: 9 nm thickness follow-up a 15-min annealing at 1000 °C, and S-A2: 17 nm thickness follow-up a 15-min annealing at 1000 °C.](image)
different phases should be perceived as indicative and not a conclusive criterion for phase stabilization, acting together with other factors influencing the formation of interfaces. In terms of formation energy (i.e., applying the “energy filter” or “energy selection criterion”), Ta$_2$O$_5$ occupies an intermediate place between the substrate Al$_2$O$_3$ and Ta$_3$N$_5$, while satisfying relatively well the topology criterion (4.3% DFT lattice mismatch between Al$_2$O$_3$ and Ta$_2$O$_5$) as well. Thus, the growth of Ta$_2$O$_5$ on the Al$_2$O$_3$ substrate appears energetically and topologically favorable. Once formed a thin layer of Ta$_2$O$_5$, the formation of Ta$_3$N$_5$ becomes even more favorable due to even better satisfied topological criterion (2.4% DFT lattice mismatch between Ta$_2$O$_5$ and Ta$_3$N$_5$). In addition, the presence of O$_2$ in the growth environment seems to contribute to a precursor selection at the edge of growing surface, which chemically and structurally favors the Ta$_3$N$_5$ phase. At this stage, the higher availability of N$_2$ precursor molecules compared to the availability of O$_2$ precursor molecules, together with presence of significant number of dangling bonds at the interface Ta$_3$N$_5$/Ta$_2$O$_5$, may mitigate the impact of the energy criterion (the formation energies of Ta$_3$N$_5$ and Ta$_2$O$_5$ reading ~1.25 eV/at and ~3.22 eV/at), thus leaving room for more impact to the topological criterion (2.4% lattice mismatch). This can further promote the growth of the orthorhombic Ta$_3$N$_5$ phase on the Ta$_2$O$_5$ seed layer.

4. Conclusion

Domain epitaxial growth of Ta$_3$N$_5$ film on single-crystal Al$_2$O$_3$(0001) substrate by reactive magnetron sputtering was achieved through the assistance of a Ta$_2$O$_5$ seed layer and a small addition of O$_2$ during film growth. The compositions and structures of both films and seed layers were well characterized by 0-20 XRD measurements, azimuthal φ-scans in grazing incidence geometry, and XPS. Without the use of both seed layer and O$_2$ in reactive gas, only metallic TaN phases, either mixture of c- and δ-TaN or β-TaN, were grown in the film. Phase purity and structure in the Ta$_3$N$_5$ phase dominated films was found to be highly sensitive to the seed layer’s thickness. The constitute of films changed from mixture of 111-oriented β-TaN and c-oriented Ta$_3$N$_5$, to c-oriented Ta$_3$N$_5$, and to polycrystalline Ta$_3$N$_5$, when varying the seed layer’s thickness from 5, to 9, to 17.0 nm. The azimuthal φ-scans shows that the c-oriented Ta$_3$N$_5$ film contained three-variant-orientation domains grown epitaxially with a and b planes parallel to m and a planes of Al$_2$O$_3$, respectively, where the epitaxial relationship can be represented as Ta$_3$N$_5$(001)/Al$_2$O$_3$(0001) and Ta$_3$N$_5$(010)/Al$_2$O$_3$(1120). As supported by DFT simulation results, the interplay between topological and energy selection criteria together with the deliberate presence of small amounts of O$_2$ in the growth environment benefited the growth of thin seed layers of orthorhombic Ta$_2$O$_5$. By the co-action of the mentioned criteria, this already grown Ta$_2$O$_5$ seed layer favored the growth of the orthorhombic Ta$_3$N$_5$ phase. In such a way, the underlying mechanism of domain epitaxial growth of Ta$_3$N$_5$ film on c-plane sapphire substrate is attributed to the interplay between favorable energetics of the compounds involved and similar atomic arrangement of Ta$_3$N$_5$(001) and beta-Ta$_2$O$_5$(011) translated in a small lattice mismatch of 2.6% and 4.5% (2.3% and 4.3%, respectively, when assessed by DFT calculations) for film/seed layer and seed layer/substrate, respectively, along in-plane orientations of Ta$_3$N$_5$(010), β-Ta$_2$O$_5$(001), and Al$_2$O$_3$(1120). Looking for proper substrate and seed layer through theoretical modelling and prediction is suggested to achieve the growth of single-crystal Ta$_3$N$_5$ epitaxial film without domains in the future.

Funding

This research was funded by Swedish Research Council (grant numbers 2018-04198 and 2021-00357), Swedish Energy Agency (grant number 46658-1), and Stiftelsen Olle Engkvist Byggmästare (grant number 197-0210) and the APC was funded by the Linköping University Library. The Swedish Government Strategic Research Area in Materials Science on Functional Materials at Linköping University (Faculty Grant SFO-Mat-LIU 2009-00971) is acknowledged for financial support.
CRediT authorship contribution statement

Jui-Che Chang: Conceptualization, Methodology, Data curation, Writing – original draft, Writing – review & editing, Jens Birchen: Conceptualization, Resources, Writing – review & editing, Funding acquisition. Gueorgui Kostov Gueorguiev: Methodology, Data curation, Writing – original draft, Writing – review & editing, Babak Rabbat: Methodology, Writing – review & editing. Grzegorz Greczynski: Methodology, Resources, Writing – review & editing. Fredrik Eriksson: Methodology, Writing – review & editing. Per Sandström: Methodology, Review – editing. Lars Hultman: Conceptualization, Methodology, Resources, Data curation, Writing – original draft, Writing – review & editing, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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[6] T. Higashi, Y. Sasaki, Y. Kawase, H. Nishiyama, M. Katayama, K. Takanabe, A. Pandey, D. Wang, Z. Mi, T.W. Hamann, Direct visualization, Methodology, Resources, Data curation, Writing – original draft, Writing – review & editing, Funding acquisition. Ching-Lien Hsiao: Conceptualization, Methodology, Resources, Data curation, Writing, – original draft, Writing – review & editing, Project administration, Funding acquisition.

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.


Metastable orthorhombic $\text{Ta}_3\text{N}_5$ thin films grown by magnetron sputter epitaxy

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