Structural and Ion Beam Analysis of Reactive Magnetron Sputtered Titanium Oxynitride Thin Films

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Abstract

TiO$_x$N$_y$ may combine the advantages of titanium oxides and nitrides in optimal conditions. Due to their physical and chemical versatility, titanium oxynitrides are gaining relevance in numerous applications such as optoelectronics, tribology and catalysis. In this study, titanium oxynitride thin film samples were grown at low sputtering pressure (1.07 Pa) on sodalime glass substrates using 99.99 % purity titanium target with argon working gas, pure nitrogen, background residual oxygen and constant sputtering power of 200 W. While other parameters were fixed at the optimum values, the deposition time was varied from 5 and 25 minutes. Rutherford backscattering (RBS) spectrometry was used to determine the stoichiometry and areal density of the films. X-ray diffractometry (XRD) and optical microscopy were used to study the structural and microstructural characteristics of the films. Variations in the elemental concentrations of the films with respect to the N/O ratio were observed based on the thickness and deposition time. Diffraction analysis indicated enhancement in crystallinity of the film with thickness, as shown from the changes in peak intensities at the preferred crystallographic orientation. Stoichiometric results showed transition of the TiN$_x$O$_y$ thin films from non-metallic oxide (TiO$_x$N$_y$) to metallic nitride (Ti$_2$N) characteristics with increase in N/Ti and N/O ratios.

Keywords
Titanium oxynitride; residual oxygen; IBA-RBS; areal density; sputtering pressure
1.0 Introduction

Strong interests in transition metal nitrides and oxynitrides are maintained due to their structural uniqueness and various applications in microelectronics, nanophotonics, corrosion and tribology. Recently, metal oxynitrides have as well shown great promise in the area of catalysis, especially in water splitting processes, mainly for the liberation of hydrogen from water. Its catalysis usage is in the direction of providing clean and renewable energy, which is arguably the most important challenge facing humanity at the moment. As a functional material, metal oxy-nitrides are more popular due to their physical and chemical adaptability (Shima et al., 1999; Moura et al., 2006; Ludtke et al., 2014). They are special group of materials that may combine the advantages of oxides and nitrides in optimal conditions, and recent studies have shown its usefulness in uv-visible light induced photocatalysis such as splitting of water into its components of hydrogen and oxygen for clean energy generation. In addition, transition-metal oxynitrides have good electrical conductivities and corrosion resistance, which makes them well suited for catalytic applications. Generally, oxynitride stabilities in air and moisture are greater than those of the pure nitrides, but with smaller band gaps than those of comparable oxides. This leads to useful optoelectronic properties. Metal oxinitrides are synthesized as thin films (Ludtke et al., 2014; Suzuki et al., 2014) and nanoparticles (Armtyage & Fender, 1974; Fuertes, 2006; Hitoki et al., 2002; Zhang et al., 2014), depending on preparatory technique and the targeted application (Orhan et al., 2002; Gao et al., 2011; Schilling et al., 2007).

Titanium oxynitride as a form of transition-metal oxynitrides is prepared using different techniques such as reactive sputtering, metal evaporation, vapour deposition, and wet chemical reaction (Rawal et al., 2013; Ajenifuja et al., 2012; Vaz et al., 2003; Miura et al., 2016; Hovish & Dauskardt, 2016). However, meeting the required stoichiometric composition in titanium oxynitride thin films is a common challenge (Kazemeini et al., 2000; Trapalis et al., 2007; Graciani et al., 2007; Braic et al., 2017). Mostly, the strategy is directed towards controlling the nitrogen-oxygen ratio in the oxynitride system, in order to achieve the required optical and structural properties. Relating to the foregoing, titanium oxynitride compounds have been shown to possess structure with intermediate properties between metallic TiN and insulating TiO₂ (Chappe et al., 2006; Rizzo et al., 2009; Braic et al., 2017). Sputtering has shown to be most resilient technique for film preparations, due to its versatility, controllability and flexibilty. In sputtering, TiOₓNᵧ is formed from reactive mixture of nitrogen and oxygen ions in a vacuum chamber containing the titanium target. Different methods have been used to initiate proper nitrogen-oxygen content in oxynitride films (Martin et al., 2001; Vaz et al., 2003; Mohamed et al., 2004; Chappe et al., 2006; Rawal et al., 2013). With proper parameter optimization, TiOₓNᵧ thin films with different structural and compositional profiles have been synthesized. Braic et al., (2017) and Hovish and Dauskardt (2016) synthesized TiOₓNᵧ and TaOₓNᵧ with varied physical properties using vacuum residual oxygen and atmospheric plasma respectively. More understanding on the use of non-conventional sources of reactive gases, such as residual oxygen and atmospheric plasma for TiOₓNᵧ preparations, and their effect on the film properties are still desirable. In this work, an optimum vacuum condition with nitrogen and residual oxygen content was utilized to prepare TiOₓNᵧ at varying deposition time. The report is presented on the relationship between the stoichiometric changes, film thickness and sputtering time based on the vacuum nitrogen-residual oxygen reactive process. Rutherford backscattering spectroscopy (RBS) was used to determine the thickness and the stoichiometric changes in...
the sputtered TiO$_{x}$N$_{y}$ films. The structural changes in the film in relation to the thickness and composition was obtained through diffraction analysis.

2.0 Materials and Methods

TiO$_{x}$N$_{y}$ thin films on sodalime glass substrates were prepared by reactive magnetron sputtering. A stainless-steel chamber was evacuated with turbo-molecular pump and a mechanical pump. The chamber was pump down to a residual vacuum close to 1.33E-3 Pa, before the release of the argon and nitrogen. The substrates were cut into the required sizes and cleaned successively with the following; methanol, acetone, de-ionized water and finally 20% HNO$_3$. For plasma generation, high purity argon atmosphere was used and the sputtering target was a 99.99% pure Ti disc (5 mm thick and of 50.8 mm diameter) positioned at an angle of about 45º relative to the static substrate platform. Pre-sputtering cleaning for Ti target was carried out in a pure argon, with the shutter placed to shield the substrates from plasma flow. Thereafter high purity nitrogen gas was released into the chamber to initiate reaction with the residual oxygen. The deposition parameters used for the preparation are shown in Table 1. The films were left to cool in the chamber before removal to avoid extraneous oxidation.

Ion beam analysis of the sputtered samples was done using NEC 5SDH 1.7 MeV Pelletron Tandem Accelerator, equipped with an RF charge exchange ion source to provide proton and helium ions. The measurement using the Rutherford backscattering spectrometry was performed using the 4He$^+$ ion beam and the incident energy was 2.2 MeV with the detector energy resolution of 12.0 KeV. The RBS spectra were obtained and the data was used to determine the stoichiometry, thickness and compositional depth profile of the films using SIMNRA (6.06) analysis software. The x-ray diffraction analysis was carried out with MD-10 Precision X-Ray Diffractometer. The samples were scanned at 2$\theta$º between 16º and 72º with CuK$\alpha$ radiation, while Profex, an x-ray diffraction analysis software was used to analyze and determine the crystallographic parameters (Döbelin & Kleeberg, 2015). Optical microscope was used to study the surface morphology and the microstructure of the films.

<table>
<thead>
<tr>
<th>Sputtering gas</th>
<th>Reactive gases</th>
<th>Power (W)</th>
<th>Time (min)</th>
<th>Base Press. (Pa)</th>
<th>Sputtering Press. (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon</td>
<td>Nitrogen, Oxygen</td>
<td>200</td>
<td>5 - 25</td>
<td>1.33 E-3</td>
<td>1.07</td>
</tr>
</tbody>
</table>

3.0 Results and Discussions

3.1 Ion Beam Analysis

The RBS spectra obtained by using 2.2 MeV 4He$^+$ ions are shown in Figs. 1(a) – (e), they were analyzed using the SIMNRA 6.06 code (Mayer, 2006; Adeoye et al., 2015). Rutherford backscattering method simultaneously provides information about the stoichiometry, thickness and the areal density of the films. SIMNRA software was used to fit the simulation over experimental data and give information regarding the stoichiometric compositions and thickness of the samples. Both the heavy element Ti, and the light elements (N and O) were detected via the backscattering process, and it is observed that the samples deposited at lowest sputtering time contained highest amount of oxygen. Due to the lightness of nitrogen and oxygen compared to the incident ion energy (2.2 MeV 4He$^+$), the signal from them were not as well resolved as that coming from the heavier Ti element. The film thickness was obtained in RBS unit (10$^{15}$ atoms/cm$^2$), and the effective composition of the films at different time are given in Table 1. The presence of
oxygen in the film was also visually observed from the dark blue colour, characteristic of titanium oxynitride, while the variations in colour of the films could be noticed in relation to the sputtering time. The colour observation is in order with recent studies (Naik et al., 2012; Ajenifuja et al., 2016; Braic et al., 2017). Braic et al. (2017) studied the effect of the level of background residual oxygen on the optical properties of the sputtered titanium oxynitride thin films. It was shown that TiO$_x$N$_y$ samples deposited under high residual oxygen level showed non-metallic (TiO$_2$) behaviour, while the films deposited when the level of residual oxygen in the background vacuum was low exhibited metallic (TiN) behaviour. In the present study, since the sputtering chamber was maintained at a relatively low working pressure, which correspond to lower nitrogen fractional flow. It was observed that the films deposited at lower sputtering time contained relatively higher amount of oxygen that those films sputtered at longer time, which indicated higher vacuum residual oxygen at the onset of sputtering. Hence, it was shown that the films prepared at deposition time of 25 minutes contained negligible amount of oxygen. The thickness (in RBS unit) and chemical composition results for the deposited TiO$_x$N$_y$ films are shown in Table 2. Studies on sputtering of metal nitride and oxynitrides showed that the most active material at very low sputtering pressure is the ionized metal target atoms (Mao et al., 2001; Ajenifuja et al., 2016; Braic et al., 2017). Increase in sputtering pressure caused an increase in the fractional flow of nitrogen, which usually result in decrease in target emission (Mao et al., 2001; Gao et al., 2011; Nirupama et al., 2010; Ji-Cheng et al., 2009). Specifically, the fixed low sputtering pressure (1.07 Pa) adopted for this experiment corresponds to the intermediate working pressure with background residual oxygen present in the chamber. From the stoichiometry of the films, it is observed that titanium ions initially dominated the sputtering chamber. Normally, in order to increase the content of nitrogen, the fractional flow needs to be increased against the fixed residual oxygen (Ajenifuja et al., 2016; Ajenifuja et al., 2018). Findings have indicated that the degree of filling of the non-metallic sub lattice of the nitride increases linearly as the nitrogen content rises, and that is why, time and partial nitrogen pressure affect the nitrogen content, and usually determine the composition of the nitride film (Fedirko & Pohrelyuk, 1995; Mao et al., 2001; Pohrelyuk et al., 2009). However, as the sputtering time increases, the flow of nitrogen and its emission intensity improves, while the residual oxygen content diminished in the chamber. It has been shown that variation of the sputtering time induces changes to the particle fluxes impacting on the substrate surface and it affects the chemical composition of the films (Roth et al., 1995; Ajenifuja et al., 2018). In this study, as the deposition time increases, there is a corresponding increase in N$_2$ emission in the plasma. The profile showing the relationship between the elemental constituents of the film in relation to the thickness is given in Fig. 3. It can be seen that as thickness increases, the oxygen composition in the films becomes diminished. Hence negligible amount of oxygen was detected in film deposited at 25 minutes. It indicated that, sputtering time did not only affect the thickness, but also the chemical composition of the films.
Figure 1: RBS Spectra for the TiOxNy on sodalime glass substrates (a) GLS, (b) TON-GL5, (c) TON-GL10, (d) TON-GL15, (e) TON-GL20, (f) TON-GL25
Table 2: Elemental composition and RBS thickness values of the film on sodalime glass substrates

<table>
<thead>
<tr>
<th>Sample</th>
<th>Deposition Time (mins)</th>
<th>RBS (10^{15} atoms/cm^2)</th>
<th>Ti</th>
<th>N</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>TON-GL5</td>
<td>5</td>
<td>655.085</td>
<td>0.735</td>
<td>0.143</td>
<td>0.122</td>
</tr>
<tr>
<td>TON-GL10</td>
<td>10</td>
<td>930.729</td>
<td>0.723</td>
<td>0.204</td>
<td>0.073</td>
</tr>
<tr>
<td>TON-GL15</td>
<td>15</td>
<td>1547.253</td>
<td>0.693</td>
<td>0.255</td>
<td>0.052</td>
</tr>
<tr>
<td>TON-GL20</td>
<td>20</td>
<td>2607.366</td>
<td>0.660</td>
<td>0.328</td>
<td>0.012</td>
</tr>
<tr>
<td>TON-GL25</td>
<td>25</td>
<td>3103.178</td>
<td>0.652</td>
<td>0.337</td>
<td>0.011</td>
</tr>
</tbody>
</table>

3.2 X-Ray Diffraction Analysis

The structural details of the magnetron sputtered TiO\textsubscript{x}N\textsubscript{y} thin films on sodalime glass at varied times of deposition, but at a fixed low sputtering pressure in a mixture of argon, nitrogen and the vacuum residual oxygen are shown in Fig. 3. The XRD parameter values obtained for the films are presented in Table 3. It is shown from the spectra that relatively thin TiO\textsubscript{x}N\textsubscript{y} films sputtered at 5 and 10 minutes barely exhibit any form of crystallinity. Meanwhile, as the thickness increase, the crystallinity of the films increases remarkably, thus exhibit well resolved peak at intermediate 2θº region (40.17° - 40.41°) corresponding to the plane (111), which is attributed to Ti phase (Glavatskikh & Gorshkov, 1992). It is shown from the sputtered films spectra intensities that (111) is the preferred orientation. A slight shift of the peaks towards higher 2θº with increase in the film thickness is observed, which is most likely due to the change in structural properties. This is in agreement with earlier studies which showed that titanium oxynitride films sputtered at different levels of vacuum residual oxygen exhibited properties ranging from non-metallic (oxide) to metallic (TiN) nature (Braic et al., 2017). In this work, vacuum residual oxygen level linearly reduces with sputtering time, and thus influenced the sputtered TiO\textsubscript{x}N\textsubscript{y} stoichiometry. In all samples, except TON-GL5, a crystalline phase with (111) reflection attributed to Ti is the only observable phase. Increase in the films Ti phase crystallization with thickness could also be linked to packing rearrangement of the impinging particles as they grew farther away from the influence of the amorphous glass substrate. It is known that substrates do have strong influence on the structural properties of thin films. The film crystallinity increases could also be related with the oxygen reduction in the film stoichiometry.
In addition, it is observed that all the spectra obtained show a broad or diffused peak at the lower 2 theta region (15 - 35º), which might be an indication of an amorphous or nanostructure TiO₂ presence. In related studies, similar broad peaks have been observed for TiO₂ nanostructures at low 2θ range, and sharp peak(s) in range assigned to (110) plane (Tang et al., 2009; Wu et al., 2002; Ranjitha et al., 2013). In line with the RBS results and in agreement with previous studies, there is an initial formations of TiOₓNᵧ reminiscent of non-metallic TiO₂ before transition to the metallic-natured crystalline TiNₓ-Oₓ, which is more of mixture of TiNₓ and Ti phases (Braic et al., 2017; Ajenifuja et al., 2018). In this study, sputtering time have strong influence on the residual oxygen, nitrogen partial pressure and sputtering mode, which have resultant effects on the film thickness, stoichiometry and structure as observed (Ajenifuja et al., 2016; Chandra et al., 2005). The sputtering pressure and time adopted remarkably favours the films transition from oxide-like TiOₓNᵧ to Ti₂N with metallic behaviour (Ajenifuja et al., 2012; Ajenifuja et al., 2016; Braic et al., 2017).

Table 3: XRD parameters for the sputtered TiOₓNᵧ thin films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Interplanar spacing, d(Å)</th>
<th>Lattice parameters, a, c (Å)</th>
<th>Orientation angle (2θº)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TON-GL5</td>
<td>2.240</td>
<td>2.950</td>
<td>4.681</td>
</tr>
<tr>
<td>TON-GL10</td>
<td>2.281</td>
<td>3.002</td>
<td>4.725</td>
</tr>
<tr>
<td>TON-GL15</td>
<td>2.222</td>
<td>2.920</td>
<td>4.661</td>
</tr>
<tr>
<td>TON-GL20</td>
<td>2.302</td>
<td>3.061</td>
<td>4.648</td>
</tr>
<tr>
<td>TON-GL25</td>
<td>2.238</td>
<td>2.934</td>
<td>4.729</td>
</tr>
</tbody>
</table>

Figure 3: XRD Spectra for the TiOₓNᵧ films on sodalime glass substrates at different thickness
3.3 Microstructural Analysis
Photomicrographs of the film samples at different thicknesses are shown in Figs. 4(a) to (d), representing TON-10 to TON-25 respectively. The images for samples deposited at lower deposition time, with relatively lower thickness are shown to be constituted of dispersed particles on the dense background. The grains are believed to be from coalescence of smaller particle and are evenly distributed on the substrates. Based on studies, at low sputtering pressure, the sputtered ions possess high mean free path, and thus impinge on the substrate with high kinetic energy which improves surface agglomeration. Since the sputtering time is increased from one sample to the other, without influencing other process parameters. Steady increase in the film thickness was obtained, which was as a result of buildup of the larger grains which makes up the superstructure. Meanwhile, with increase in the sputtering time, a differentiable changes are observed in the surface morphologies, in terms of micro-particle distribution and population. For example sample TON-10 consists of highly dispersed globular particles, which is a bit similar to TON-15 shown in Fig. 4(b). For all the films being sputtered at low pressure, the mean free path of the particles would remain nearly constant in all the experiments, but the particles accumulation changed with time. Therefore, a linear increase in thickness is shown, but with changes in the films composition. Due to the instrumental limitation of the microscope, it is not possible to see beyond the very topmost morphology of most of the samples, hence, an initial formation of first relatively smooth layer is assumed and then gradual accumulation of the granular crystallites. The main differences identified between the films based on thickness are the appearance of particles and surface uniformity, such that thicker films microstructure appears closely parked.

![Figure 4: Optical micrograph of the films on glass substrates (a) TON-10, (b) TON-15, (c) TON-20 and (d) TON-25](image-url)
Conclusions

TiO$_x$N$_y$ thin films of thickness ranging from 655.085 to 3103.178 x $10^{15}$ atoms/cm$^2$ were sputtered on sodalime glass substrates at relatively low sputtering in the presence of nitrogen and vacuum residual oxygen as reactive gases. With ion beam analysis, the film thickness and stoichiometry was determined. The lattice parameters, interplanar spacing and film crystallinity were observed to change with thickness and sputtering time. Meanwhile, sputtered film images showed evolution in microstructural properties. For relatively thin samples deposited at 5 and 10 minutes, no distinct crystallographic peak was detected, however, as the thickness increases, the film exhibited strong reflections corresponding to (111) planar orientation, which as attributed to hexagonal titanium phase. With consistency in the observed reflection intensity with film thickness, it indicates that it is the preferred orientation for the phase. It is shown that sputtering time have a strong influence on the residual oxygen, nitrogen partial pressure and sputtering mode. Hence, the fixed sputtering pressure and the varied time adopted remarkably favours the films transition from oxide TiO$_x$N$_y$ to metallic Ti$_2$N. With proper sputtering time and pressure control, the vacuum residual oxygen was utilized in a Ti-N system to prepared TiO$_x$N$_y$ thin films with different physical and chemical properties.

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References


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