Ta–Zr–N Thin Films Fabricated through HIPIMS/RFMS Co-Sputtering

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Abstract: Ta–Zr–N thin films were fabricated through co-deposition of radio-frequency magnetron sputtering and high-power impulse magnetron sputtering (HIPIMS/RFMS co-sputtering). The oxidation resistance of the fabricated films was evaluated by annealing the samples in a 15-ppm O₂-N₂ atmosphere at 600 °C for 4 and 8 h. The mechanical properties and surface roughness of the as-deposited and annealed thin films were evaluated. The results indicated that the HIPIMS/RFMS co-sputtered Ta–Zr–N thin films exhibited superior mechanical properties and lower surface roughness than did the conventional direct current-sputtered Ta–Zr–N thin films and HIPIMS-fabricated ZrNₓ thin films in both the as-deposited and annealed states.

Keywords: annealing; HIPIMS; mechanical properties; oxidation resistance

1. Introduction

Ta–Zr–N coatings have been employed as protective coatings against wear for biomedical implants [1,2] and as diffusion barrier layers in Cu metallization [3]. Ta-rich Ta–Zr–N coatings exhibited enhanced toughness with high hardness [4,5]. In a previous study [6], low-Zr-content Ta₁₋ₓZrₓNᵧ thin films (x = 0–0.17, y = 0.86–1.03) fabricated through conventional reactive direct-current (DC) magnetron co-sputtering exhibited desirable mechanical properties and a restricted increase in surface roughness from 0.9–1.5 nm to 1.2–1.7 nm after annealing at 600 °C in a 15-ppm O₂-N₂ atmosphere for 4 h. The chemical inertness of these films against commercial moldable SiO₂–B₂O₃–BaO-based glass after 500 thermal cycles was experimentally confirmed. Thermal cycling annealing at 270 °C and 600 °C in a 15-ppm O₂-N₂ atmosphere was a realistic mass production process [7,8]. The smoothing mechanism of coating surfaces is a crucial factor when Ta–Zr–N thin films are deposited as the protective coatings on glass molding dies. High-power pulsed magnetron sputtering (also called high-power impulse magnetron sputtering (HIPIMS) [9,10]) has broadened the operating window of magnetron sputtering. HIPIMS was proposed as a method for growing high-quality films with dense structure, smooth morphology, and excellent adhesion [11], and has attracted substantial industry and research interest because of its potential use in such applications as wear resistance [11,12] and electric coatings [13]. However, despite its superiority, the mechanism underlying HIPIMS is complex because many factors—particularly pulse parameters—affect the deposition process. The low deposition rate in the HIPIMS process became a drawback for the commercial applications [10,14]. Therefore, hybrid processes, such as HIPIMS/DCMS (direct-current magnetron co-sputtering) [15] and HIPIMS/AIP (arc ion plating) [16] were utilized. In this study, co-deposition of radio-frequency magnetron sputtering and HIPIMS (hereafter, HIPIMS/RFMS co-sputtering) was used to improve the
surface quality (decrease the surface roughness) of Ta–Zr–N thin films, and its effects on the mechanical properties and oxidation resistance of the films were investigated.

2. Materials and Methods

An HIPIMS/RFMS co-sputtering system (Figure 1) was employed to deposit Ta–Zr–N thin films on silicon substrates. A 99.95% pure Ta target was connected to an RF power generator (13.56 MHz), and a 99.9% pure Zr target was connected to a SPIK2000A pulse power supply (SPIK 2000A; Shen Chang Electric Co., Taipei, Taiwan) operated in the unipolar negative mode at a constant power of 400 W. Both targets were 76.2 mm in diameter, and tilted to the vertical axis. The pulse on-time, \( t_{on} \), and pulse off-time, \( t_{off} \), were kept constant at 100 and 3900 \( \mu \)s, respectively. The duty cycle \((t_{on}/t_{on}+t_{off}) \times 100\%\) was maintained at 2.5%. The substrate-to-target vertical distance was 12 cm, and the chamber was pumped to a base pressure of 6.7 \( \times 10^{-4} \) Pa. The working pressure was maintained at approximately 0.67 Pa by flowing an Ar and N\(_2\) \((\text{Ar}:\text{N}_2 = 9:1)\) gas mixture into the chamber. The substrate holder was rotated at 10 rpm during the process. A pulse bias voltage of −50 V was applied to the substrate holder, and the coatings were deposited at 400 °C. Table 1 lists the sputtering powers employed to fabricate the Ta–Zr–N thin films; the deposition times were altered to achieve coating thicknesses of 1217–1279 nm. The Ta–Zr–N thin films were further annealed at 600 °C for 4 and 8 h in a 15-ppm O\(_2\)-N\(_2\) atmosphere in a quartz tube furnace.

Figure 1. Schematic image of the radio-frequency magnetron sputtering and high-power impulse magnetron sputtering (HIPIMS/RFMS) co-sputtering equipment.

Table 1. Sputter parameters for depositing Ta–Zr–N thin films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>RF Power (W_{Ta})</th>
<th>HIPIMS Power (W_{Zr})</th>
<th>Zr Power Density (W/cm(^2))</th>
<th>Deposition Time (min)</th>
<th>Coating Thickness (nm)</th>
<th>Deposition Rate (nm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>100</td>
<td>400</td>
<td>1656</td>
<td>210</td>
<td>1217</td>
<td>5.80</td>
</tr>
<tr>
<td>B</td>
<td>200</td>
<td>400</td>
<td>1632</td>
<td>140</td>
<td>1238</td>
<td>8.84</td>
</tr>
<tr>
<td>C</td>
<td>300</td>
<td>400</td>
<td>1576</td>
<td>105</td>
<td>1279</td>
<td>12.18</td>
</tr>
<tr>
<td>D</td>
<td>400</td>
<td>400</td>
<td>1500</td>
<td>85</td>
<td>1253</td>
<td>14.75</td>
</tr>
</tbody>
</table>

Chemical composition analysis was conducted by using a field-emission electron probe microanalyzer (FE-EPMA, JXA-8500F, JEOL, Akishima, Japan) on the surface of the samples. The film and oxide scale thicknesses were evaluated by field emission scanning electron microscopy (FE-SEM, S4800, Hitachi, Tokyo, Japan) on the fracture surface of the samples, initiated from the backside of Si wafers. A conventional X-ray diffractometer (XRD, X’Pert PRO MPD, PANalytical, Almelo, The Netherlands) with Cu K\(\alpha\) radiation was adopted to identify the phases of the coatings, using the grazing incidence technique with an incidence angle of 1°. The nanostructure of the coatings and scales was further examined using transmission electron microscopy (TEM, JEM-2100F, JEOL, Akishima, Japan) at a 200-kV accelerating voltage. TEM samples were prepared by applying a focused ion beam system (FEI Nova 200, Hillsboro, OR, USA) at an accelerating voltage of 30 kV with a gallium ion
source. A Pt layer was deposited to protect the free surface during sample preparation. The surface nanoindentation hardness values of Ta$_{1-x}$Zr$_x$N$_y$ coatings were measured with a nanoindentation tester (TI-900 Triboindenter, Hysitron, Eden Prairie, MN, USA). The nanoindentor was equipped with a Berkovich diamond probe tip. The applied load was controlled to exhibit an indentation depth of 100 nm. The loading, holding, and unloading times were 5 s each. The nanoindentation hardness and reduced elastic modulus $E_r$ of each indent were calculated based on the Oliver and Pharr method [17].

The elastic modulus, $E$, of a film can be determined from:

$$\frac{1}{E_r} = \frac{1 - \nu_i^2}{E_i} + \frac{1 - \nu_f^2}{E_f}$$

where $E$, $\nu$, $E_i$, and $\nu_i$ are the elastic modulus and Poisson’s ratio of the film and indenter, using $\nu = 0.25$, $E_i = 1141$ GPa, and $\nu_i = 0.07$ [18], respectively. The surface roughness values of the coatings were evaluated by using an atomic force microscope (AFM, Dimension 3100 SPM, NanoScope IIIa, Veeco, New York, NY, USA). The scanning area of each image was set at 5 µm x 5 µm with a scanning rate of 1.0 Hz. The residual stress of the films measured by the curvature method was calculated using Stoney’s equation [19].

3. Results and Discussion

3.1. As-Deposited Ta–Zr–N Thin Films

Table 2 lists the elemental compositions of the as-deposited Ta–Zr–N thin films prepared through HIPIMS/RFMS co-sputtering. The Ta content in the Ta–Zr–N thin films increased with increasing Ta target power. The oxygen content in the as-deposited states were 1.0–2.3 at %. The samples were designated in the form Ta$_{1-x}$Zr$_x$N$_y$, as follows: Ta$_{0.84}$Zr$_{0.16}$N$_{0.40}$, Ta$_{0.81}$Zr$_{0.19}$N$_{0.52}$, Ta$_{0.58}$Zr$_{0.42}$N$_{0.59}$, and Ta$_{0.33}$Zr$_{0.67}$N$_{0.68}$. The atomic ratio of N/(Ta + Zr) increased from 0.40 to 0.52, 0.59, and 0.68 as the power of the Ta target increased from 100 to 200, 300, and 400 W, respectively. The deposition parameters were adjusted to fabricate thin films of similar thicknesses (Table 1); the Ta$_{0.84}$Zr$_{0.16}$N$_{0.40}$, Ta$_{0.81}$Zr$_{0.19}$N$_{0.52}$, Ta$_{0.58}$Zr$_{0.42}$N$_{0.59}$, and Ta$_{0.33}$Zr$_{0.67}$N$_{0.68}$ thin films were 1253, 1279, 1238, and 1217 nm thick, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Annealing Time (h)</th>
<th>Chemical Composition (at %)</th>
<th>Atomic Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ta</td>
<td>Zr</td>
</tr>
<tr>
<td>A</td>
<td>0</td>
<td>19.0 ± 0.0</td>
<td>39.1 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>17.5 ± 0.4</td>
<td>35.9 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>16.3 ± 0.4</td>
<td>33.6 ± 0.5</td>
</tr>
<tr>
<td>B</td>
<td>0</td>
<td>36.3 ± 0.1</td>
<td>26.1 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>29.3 ± 0.5</td>
<td>23.0 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>27.5 ± 0.5</td>
<td>21.8 ± 0.1</td>
</tr>
<tr>
<td>C</td>
<td>0</td>
<td>52.5 ± 0.2</td>
<td>12.5 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>35.8 ± 0.4</td>
<td>16.1 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>33.0 ± 0.3</td>
<td>14.9 ± 0.3</td>
</tr>
<tr>
<td>D</td>
<td>0</td>
<td>59.3 ± 0.7</td>
<td>11.0 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>36.3 ± 0.5</td>
<td>11.1 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>35.3 ± 0.7</td>
<td>11.1 ± 0.2</td>
</tr>
</tbody>
</table>

Figure 2 shows the grazing-incident XRD patterns of the as-deposited Ta–Zr–N thin films. Although the atomic ratio of N/(Ta + Zr) deviated from the stoichiometric value of 1, the Ta$_{0.81}$Zr$_{0.19}$N$_{0.52}$, Ta$_{0.58}$Zr$_{0.42}$N$_{0.59}$, and Ta$_{0.33}$Zr$_{0.67}$N$_{0.68}$ thin films exhibited a face-centered cubic (fcc) structure. For transition-metal-nitride coatings, N vacancy concentrations can be up to 50% [20]. Matenoglo et al. [21] reported that the ternary transition metal nitrides Ta$_x$Me$_{1-x}$N (Me = Ti, Zr, Hf, Nb, Ta, Mo, W) formed solid solutions over the entire x range (0 < x < 1) and that they were stable in the rock-salt structure regardless of the valence electron configuration of its constituent metals.
Furthermore, the reflections shift left as Zr content in the Ta–Zr–N thin films increases because the lattice parameters of standard cubic TaN and ZrN are 0.4340 nm (ICDD 49-1283) and 0.4577 nm (ICDD 35-0753), respectively. By contrast, the Ta$_{0.84}$Zr$_{0.16}$N$_{0.40}$ thin film exhibited a mixture of hexagonal β-Ta[89-1545], hexagonal γ-Ta$_2$N (ICDD 26-0985), and cubic ZrN phases, which is attributable to the severe lack of N content in the thin films. Since the standard Gibbs free energies of the metal nitride formation of TaN, Ta$_2$N, and ZrN at 400 °C are −391,001 J/(mol of N$_2$), −420,567 J/(mol of N$_2$), and −602,902 J/(mol of N$_2$) [22], respectively, ZrN formed preferentially, followed by Ta$_2$N. The deficiency of N in the Ta$_{0.84}$Zr$_{0.16}$N$_{0.40}$ coating resulted in that an excess Ta remained in the β-Ta phase but no N atoms were available to form TaN. The N content of the Ta–Zr–N thin films decreased with increasing power supplied on the Ta target ($W_{Ta}$), which was attributed to the re-sputtering of N atoms from the surface resulting from the increasing energy of bombarding ions [23,24].

**Figure 2.** XRD patterns of as-deposited Ta–Zr–N thin films prepared on Si substrates.

Figures 3 and 4 present the AFM and cross-sectional SEM images of the as-deposited Ta–Zr–N thin films, respectively. The Ta$_{0.84}$Zr$_{0.16}$N$_{0.40}$, Ta$_{0.33}$Zr$_{0.67}$N$_{0.68}$, and Ta$_{0.58}$Zr$_{0.42}$N$_{0.59}$ thin films exhibited a smooth surface and a dense structure with a surface roughness of 0.4–0.5 nm (Table 3). By contrast, the Ta$_{0.33}$Zr$_{0.67}$N$_{0.68}$ thin film exhibited a coarser columnar structure with a high surface roughness of 2.5 nm. The film structure transition from columnar to dense non-columnar was attributed to the increasing energy of bombarding ions [25,26].

**Table 3.** Film and oxide scale thicknesses, surface roughness, mechanical properties, elastic recovery, and residual stress values of as-deposited and 600 °C-annealed Ta–Zr–N thin films prepared on Si substrates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_A$ (h)</th>
<th>Thickness (nm)</th>
<th>Surface Roughness</th>
<th>$H$ (GPa)</th>
<th>$E$ (GPa)</th>
<th>$H/E^2$</th>
<th>$W_e$ (GPa)</th>
<th>Residual Stress (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta$<em>{0.33}$Zr$</em>{0.67}$N$_{0.68}$</td>
<td>0</td>
<td>1217</td>
<td>0</td>
<td>30.2 ± 0.9</td>
<td>306 ± 7</td>
<td>0.30</td>
<td>67</td>
<td>−4.18 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1176</td>
<td>0</td>
<td>29.3 ± 0.2</td>
<td>283 ± 4</td>
<td>0.28</td>
<td>63</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>979</td>
<td>4</td>
<td>3.55 ± 0.58</td>
<td>235 ± 7</td>
<td>0.13</td>
<td>56</td>
<td>−</td>
</tr>
<tr>
<td>Ta$<em>{0.58}$Zr$</em>{0.42}$N$_{0.59}$</td>
<td>0</td>
<td>1238</td>
<td>0</td>
<td>35.0 ± 0.6</td>
<td>311 ± 3</td>
<td>0.44</td>
<td>73</td>
<td>−6.17 ± 0.47</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1208</td>
<td>62</td>
<td>0.80 ± 0.00</td>
<td>262 ± 3</td>
<td>0.25</td>
<td>62</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1131</td>
<td>151</td>
<td>1.65 ± 0.28</td>
<td>268 ± 4</td>
<td>0.21</td>
<td>59</td>
<td>−</td>
</tr>
<tr>
<td>Ta$<em>{0.81}$Zr$</em>{0.19}$N$_{0.52}$</td>
<td>0</td>
<td>1279</td>
<td>0</td>
<td>35.5 ± 0.4</td>
<td>299 ± 3</td>
<td>0.50</td>
<td>76</td>
<td>−4.84 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1192</td>
<td>136</td>
<td>1.06 ± 0.10</td>
<td>254 ± 6</td>
<td>0.15</td>
<td>56</td>
<td>−3.46 ± 0.19</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1149</td>
<td>195</td>
<td>1.40 ± 0.24</td>
<td>244 ± 3</td>
<td>0.13</td>
<td>50</td>
<td>−2.80 ± 0.01</td>
</tr>
<tr>
<td>Ta$<em>{0.84}$Zr$</em>{0.16}$N$_{0.40}$</td>
<td>0</td>
<td>1253</td>
<td>0</td>
<td>3.7 ± 0.01</td>
<td>258 ± 11</td>
<td>0.49</td>
<td>75</td>
<td>−4.65 ± 0.20</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1164</td>
<td>131</td>
<td>0.54 ± 0.02</td>
<td>251 ± 3</td>
<td>0.14</td>
<td>56</td>
<td>−2.60 ± 0.17</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1071</td>
<td>221</td>
<td>1.15 ± 0.29</td>
<td>235 ± 2</td>
<td>0.11</td>
<td>52</td>
<td>−2.80 ± 0.00</td>
</tr>
</tbody>
</table>

Note: $T_A$: Annealing time.
Using the same sputtering system [30], the HIPIMS-fabricated ZrN structure [27]. By contrast, the elastic modulus of the Ta$_{0.84}$Zr$_{0.16}$N$_{0.40}$ films indicate substrates.-crystalline Ta$_{0.84}$Zr$_{0.16}$N$_{0.40}$ thin films, respectively. The elastic recovery of the as-deposited Ta–Zr–N thin films exhibited a level of 67%–76%. In a previous study using the same sputtering system [30], the HIPIMS-fabricated ZrNx thin films (x = 0.65–0.78) exhibited a resistance to plastic deformation [28], and were 0.49, 0.50, 0.44, and 0.30 for the Ta$_{0.84}$Zr$_{0.16}$N$_{0.40}$, Ta$_{0.81}$Zr$_{0.19}$N$_{0.52}$, Ta$_{0.58}$Zr$_{0.42}$N$_{0.59}$, and Ta$_{0.33}$Zr$_{0.67}$N$_{0.68}$ thin films, respectively. The elastic recovery $W_e$ [29] of the as-deposited Ta–Zr–N thin films exhibited a level of 67%–76%. In a previous study using the same sputtering system [30], the HIPIMS-fabricated ZrN$_x$ thin films (x = 0.65–0.78) exhibited...

Figure 3. Atomic force microscopy (AFM) images of as-deposited Ta–Zr–N thin films prepared on Si substrates. (a) Ta$_{0.84}$Zr$_{0.16}$N$_{0.40}$; (b) Ta$_{0.81}$Zr$_{0.19}$N$_{0.52}$; (c) Ta$_{0.58}$Zr$_{0.42}$N$_{0.59}$; (d) Ta$_{0.33}$Zr$_{0.67}$N$_{0.68}$.

Figure 4. Cross-sectional SEM images of as-deposited Ta–Zr–N thin films prepared on Si substrates. (a) Ta$_{0.84}$Zr$_{0.16}$N$_{0.40}$; (b) Ta$_{0.81}$Zr$_{0.19}$N$_{0.52}$; (c) Ta$_{0.58}$Zr$_{0.42}$N$_{0.59}$; (d) Ta$_{0.33}$Zr$_{0.67}$N$_{0.68}$.
a hardness of 26–27 GPa, a Young’s modulus of 260–290 GPa, a residual stress of -4.2 – 5.2 GPa, and a surface roughness of approximately 0.5 nm in the as-deposited state. The introduction of Ta into the ZrN-based thin films evidently raised the hardness values and maintained similar Young’s modulus levels.

Aouadi [2] reported the mechanical properties of overstoichiometric Ta–Zr–N films deposited by reactive unbalanced magnetron DC sputtering, which exhibited a hardness of <30 GPa with a wide range of Ta/(Ta + Zr) ratios (0.16–0.78) except for the film with a Ta/(Ta + Zr) ratio of 0.29, which exhibited a sudden increased hardness of 37 GPa attributed to solid solution hardening and limited segregation of solutes at grain boundaries. Abadias et al. [4,5] reported a hardness level of ~30 GPa for Zr_{x=0.51–0.78}N films (x = 0.51–0.78) prepared using DC magnetron co-sputtering. The residual stress was -4.65, -4.84, -6.17, and -4.18 GPa for the as-deposited Ta_{0.84}Zr_{0.16}N_{0.40}, Ta_{0.81}Zr_{0.19}N_{0.52}, Ta_{0.58}Zr_{0.42}N_{0.59}, and Ta_{0.33}Zr_{0.67}N_{0.68} thin films (Table 3), respectively. These values were more negative than those with similar Zr/(Ta + Zr) ratios reported in our previous study [6], in which the residual stress of the DC-sputtered Ta_{1–x}Zr_{x}N_y thin films (x = 0.17–0.72, y = 1.03–1.09) ranged from 0 to -2.11 GPa. Residual stress affects the hardness of the coatings; in other words, compressive stress increases coating hardness, whereas tensile stress reduces it [31]. The as-deposited Ta–Zr–N thin films with a wide Zr/(Ta + Zr) ratio range of 0.16–0.67 fabricated in this study exhibited nanoindentation hardnesses of 30–35 GPa, superior to the 22–26 GPa reported for the DC-sputtered Ta_{0.83}Zr_{0.17}N_{1.03}, Ta_{0.59}Zr_{0.41}N_{1.09}, and Ta_{0.28}Zr_{0.72}N_{1.05} thin films [6].

3.2. Ta–Zr–N Thin Films Annealed in a 15-ppm O_2–N_2 Atmosphere at 600 °C

Table 2 lists the elemental compositions of the Ta–Zr–N thin films annealed at 600 °C in a 15-ppm O_2–N_2 atmosphere for 4 and 8 h. The atomic ratios of Zr/(Ta + Zr) of the annealed Ta_{0.58}Zr_{0.42}N_{0.59} and Ta_{0.33}Zr_{0.67}N_{0.68} thin films retained their values in the as-deposited states (0.42 and 0.67, respectively), whereas the Zr/(Ta + Zr) ratios of the annealed Ta_{0.84}Zr_{0.16}N_{0.40} and Ta_{0.81}Zr_{0.19}N_{0.52} thin films increased from 0.16 to 0.23 and from 0.19 to 0.31, respectively. By contrast, the atomic ratios of Ta/Zr of the DC-sputtered Ta_{1–x}Zr_{x}N_y thin films (x = 0.05–0.72, y = 0.97–1.05) [6] retained their preannealing values after annealing at 600 °C in 15-ppm O_2–N_2 for 4 h. Moreover, the DC-sputtered Ta_{1–x}Zr_{x}N_y thin films were near-stoichiometric, whereas the Ta–Zr–N thin films in this study were understoichiometric. Furthermore, the DC-sputtered Ta_{1–x}Zr_{x}N_y thin films with a higher Zr content gathered a higher O content after annealing, which was in contrast to the Ta–Zr–N thin films prepared in this study. The HIPIMS/RFMS-fabricated Ta–Zr–N thin films with a lower Zr content gathered a higher O content after annealing. These results implied that the variations of Zr/(Ta + Zr) ratio and O content of the annealed Ta–Zr–N thin films in this study were caused by nonstoichiometric compositions, which contributed a high degree of nonmetal site vacancies in the nitride structure; therefore, O quickly diffused inward. Conversely, Zr preferentially diffused outward and reacted with O to form ZrO_2 around the near-surface region because Zr possesses a lower mass than Ta does, and because the standard Gibbs free energies of the metal oxide formations of ZrO_2 and Ta_2O_5 at 600 °C are -931,249 and -663,572 J per mole of oxygen molecules [22], respectively. Since ZrO_2 was the dominant oxide and is not volatile, and the chemical composition analysis was conducted on the surface, the Zr/(Ta + Zr) ratios maintained and increased for the high- and low-Zr-content films, respectively. The N/(Ta + Zr) ratios of the annealed Ta_{0.81}Zr_{0.19}N_{0.52}, Ta_{0.58}Zr_{0.42}N_{0.59}, and Ta_{0.33}Zr_{0.67}N_{0.68} thin films decreased slightly due to the replacement of N by O in the beginning of oxidation, whereas the N/(Ta + Zr) ratio of the annealed Ta_{0.84}Zr_{0.16}N_{0.40} thin films maintained a level similar to that at the as-deposited state due to the high degree of understoichiometric structure.

The XRD patterns of the 4-h-annealed Ta–Zr–N thin films (data not shown) did not differ from those of the corresponding as-deposited thin films. Figure 5 presents the XRD patterns of the 8-h-annealed Ta–Zr–N thin films, which also exhibited reflections similar to those of the as-deposited thin films except that a wide diffraction reflection appeared at the 2θ angle of approximately 30° for the Ta_{0.33}Zr_{0.67}N_{0.68} thin film, which is attributable to the formation of a surface oxide scale.
The lattice fringes of (200) and (111) planes in the columnar nitride structure show d-spacings of 0.33, 0.40, and 0.68 nm, respectively. Figure 7a shows the cross-sectional TEM image of the 8-h-annealed Ta0.84Zr0.16N0.40 thin film, whose selected area diffraction pattern exhibits an fcc phase. The high-resolution image (Figure 7b) of the outermost surface region exhibits an amorphous oxide scale of approximately 13 nm. Lattice fringes with d-spacings of 0.224 and 0.259 nm, which respectively correlate to the stacking of (200) and (111) planes, were identified beneath the outermost surface oxide region. The dark-field image corresponding to the (111) diffraction spot in Figure 7a reveals a fine columnar structure with a width of 30 nm (Figure 7c). Figure 8a shows the cross-sectional TEM image of the 8-h-annealed Ta0.33Zr0.67N0.68 thin film, whose columnar structure and diffraction pattern are more evident than those of the annealed Ta0.58Zr0.42N0.59 thin film. Figure 8b indicates that crystalline ZrO2 domains were observed in the surface oxide scale of the annealed Ta0.33Zr0.67N0.68 thin film. The lattice fringes of (200) and (111) planes in the columnar nitride structure show d-spacings of 0.229 and 0.263 nm, respectively. Figure 8c exhibits the dark-field image corresponding to the (111) diffraction spot in Figure 8a and reveals a coarser columnar width of 95 nm. The oxide scales of Ta0.84Zr0.16N0.40 and Ta0.81Zr0.19N0.52 were inferred to be amorphous because no oxide reflections were observed in their XRD patterns.

Figure 5. XRD patterns of the Ta–Zr–N thin films after annealing at 600 °C in 15 ppm O2–N2 for 8 h.

Figure 6. Cross-sectional SEM images of the Ta–Zr–N thin films after annealing at 600 °C in 15 ppm O2–N2 for 8 h. (a) Ta0.84Zr0.16N0.40; (b) Ta0.81Zr0.19N0.52; (c) Ta0.58Zr0.42N0.59; (d) Ta0.33Zr0.67N0.68.
Although the hardness measurement of the annealed thin films included the contribution of surface hardnesses of 32–35 GPa, Young’s moduli of 258–311 GPa, roughness from 0.5 to 3–6 nm.

To the formation of crystalline ZrO\textsubscript{2} scales, which was accompanied by an increase in the surface roughness from 0.5 to 3–6 nm.

The vital characteristics of the protective coatings on glass molding dies were high hardness, low surface roughness, and chemical inertness against moldable optical glasses [6,8,32,33]. The formation of amorphous surface oxide scales on high-Ta-content Ta–Zr–N thin films restricted the increase in surface roughness relative to that of crystalline oxide scales formed on high-Zr-content Ta\textsubscript{0.33}Zr\textsubscript{0.67}N\textsubscript{0.68} thin films (Table 3). Since the hardness values of the moldable optical glasses ranged from 3.2 to 7.0 GPa, the protective coatings with a hardness higher than 10 GPa were preferred [8]. Although the hardness measurement of the annealed thin films included the contribution of surface oxide scale, this hardness value implied a realistic strength against the glasses in the molding process. The nanoindentation hardnesses decreased to 20.9, 21.5, 25.7, and 28.3 GPa for the 4-h-annealed Ta\textsubscript{0.84}Zr\textsubscript{0.16}N\textsubscript{0.40}, Ta\textsubscript{0.81}Zr\textsubscript{0.19}N\textsubscript{0.52}, Ta\textsubscript{0.38}Zr\textsubscript{0.42}N\textsubscript{0.59}, and Ta\textsubscript{0.33}Zr\textsubscript{0.67}N\textsubscript{0.68} thin films (Table 3), respectively; furthermore, the nanoindentation hardnesses decreased to 18.0, 19.5, 24.8, and 19.3 GPa after 8 h of annealing, respectively. Both the $H^3/E^2$ ratio and elastic recovery $W_e$ exhibited decreased trends with increasing the annealing time due to the formation of surface oxide.

The residual stress of annealed Ta\textsubscript{0.84}Zr\textsubscript{0.16}N\textsubscript{0.40} and Ta\textsubscript{0.81}Zr\textsubscript{0.19}N\textsubscript{0.52} thin films decreased to a range of −2.6 to −3.5 GPa (Table 3). The annealed Ta\textsubscript{0.38}Zr\textsubscript{0.42}N\textsubscript{0.59} and Ta\textsubscript{0.33}Zr\textsubscript{0.67}N\textsubscript{0.68} thin films exhibited local detachment after annealing; hence, the residual stress could not be evaluated. In a previous study [30], the nanoindentation hardness values of the HIPIMS-fabricated ZrN\textsubscript{x} thin films declined from 26–27 GPa to less than 10 GPa after they were annealed at 600 °C in 15 ppm O\textsubscript{2}–N\textsubscript{2} for 2 h owing to the formation of crystalline ZrO\textsubscript{2} scales, which was accompanied by an increase in the surface roughness from 0.5 to 3–6 nm.

4. Conclusions

We reported the preparation of understoichiometric Ta–Zr–N thin films with atomic ratios (N/(Ta + Zr)) of 0.40–0.68 through HIPIMS/RFMS co-sputtering. The as-deposited high-Ta-content Ta–Zr–N thin films Ta\textsubscript{0.84}Zr\textsubscript{0.16}N\textsubscript{0.40}, Ta\textsubscript{0.81}Zr\textsubscript{0.19}N\textsubscript{0.52}, and Ta\textsubscript{0.38}Zr\textsubscript{0.42}N\textsubscript{0.59} exhibited nanoindentation hardnesses of 32–35 GPa, Young’s moduli of 258–311 GPa, $H^3/E^2$ values of 0.44–0.50 GPa,
elastic recovery of 73%–76%, and surface roughnesses of 0.4–0.5 nm. The HIPIMS technique helps to fabricate dense and smooth thin films. After annealing at 600 °C in a 15-ppm O2-N2 atmosphere for 4 h, the nanoindentation hardnesses decreased to 21–26 GPa and the surface roughnesses increased to 0.5–1.1 nm. The nanoindentation hardnesses further decreased to 18–25 GPa and the surface roughnesses further increased to 1.2–1.6 nm after 8 h of annealing. The introduction of Ta into the HIPIMS-fabricated ZrN thin films evidently raised the hardness values in the as-deposited state and varied the oxide scale to be a ZrO2-dominant amorphous layer after annealing; the amorphous layer decreased the oxidation rate and reduced the declining trend of the hardness during annealing. Amorphous surface oxide scales restricted an increase in surface roughness. The HIPIMS/RFMS-co-sputtered Ta–Zr–N thin films exhibited a nanoindentation hardness of 30–35 GPa with a Zr/(Ta + Zr) ratio range of 0.16–0.67; this range was wider than those of the conventional DC-sputtered Ta–Zr–N thin films with a hardness >30 GPa.

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