

# Article Characterization of ZrBSiTaN<sub>x</sub> Films

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Abstract: In this study, ZrBSiTa and (ZrBSiTa)N<sub>x</sub> films were deposited on silicon wafers through direct current magnetron cosputtering. The nitrogen flow ratio  $(R_{N2})$  of the reactive gas and the sputter power applied to the Si target ( $P_{Si}$ ) were the variables in the fabricating processes. The influence of the N and Si contents on the mechanical properties, thermal stability, and oxidation behavior of the ZrBSiTa and (ZrBSiTa)N $_{x}$  films were investigated. All the as-fabricated films exhibited amorphous structures. The  $R_{N2}$  set at 0.1, 0.2, and 0.4 caused the ZrBSiTaN<sub>x</sub> films to exhibit high N contents of 52-55, 62-64, and 63-64 at.%, respectively. The Si content of the ZrBSiTa films increased from 0 to 42 at.% as  $P_{Si}$  increased from 0 to 150 W, and this was accompanied by decreases in hardness and Young's modulus values from 19.1 to 14.3 GPa and 264 to 242 GPa, respectively. In contrast, the increase in Si content of the (ZrBSiTa)N<sub>x</sub> films from 0 to 21 at.% increased the hardness from 11.5 to 14.0 GPa, and Young's modulus from 207 to 218 GPa. Amorphous BN and  $SiN_x$  phases in the (ZrBSiTa)N<sub>x</sub> films varied the structural and mechanical properties. The thermal stability of the (ZrBSiTa)N<sub>x</sub> films was evaluated by annealing at 800–900  $^{\circ}$ C for 10–30 min in Ar. The oxidation behavior of the (ZrBSiTa)N<sub>x</sub> films was evaluated in the ambient air at 800  $^{\circ}$ C for 0.5–24 h. The amorphous (ZrBSiTa)N<sub>x</sub> films with a high Si content had high thermal stability and oxidation resistance.

**Keywords:** mechanical properties; multicomponent alloys; oxidation behavior; residual stress; thermal stability; transition metal boride films

# 1. Introduction

Si-contained amorphous and nanocomposite transition metal (TM) nitride films have been developed due to their outstanding antioxidative [1–4] and anticorrosive properties [5–8]. One of the vital characteristics of amorphous materials is the lack of grain boundary. Grain boundaries with high defect density provide diffusion paths for elements in crystalline materials, whereas the lack of grain boundaries for amorphous structures improve the diffusion resistance of protective coatings [9–11]. Amorphous nitride thin films have been utilized as diffusion barriers in microelectronics [12–14], and oxidationresistant coatings for protective purposes at elevated temperatures [11,15-18]. The thermal stability of amorphous material in inert gas is crucial in applications such as diffusion barriers. Doping of Si or B into TM nitrides stabilizes the amorphous or nanocomposite structures [19–21]. Musil et al. [16] reported that ZrSiN films with a Si content > 25 at.% formed a stable amorphous structure when annealed at >1000 °C. The formation of nonvolatile silicon oxide (SiO<sub>x</sub>) improves the antioxidative properties of TM–Si–N films at elevated temperatures [11,17,18]. However, the mechanical properties of TM–Si–N films decline with increasing Si content because of a high volume ratio of the amorphous phase. TM boride thin films have been developed to replace TM nitride thin films in various applications [22–25]. Bakhit et al. [26] stated that  $Zr_{1-x}Ta_xB_y$  thin films had a hardness of 42 GPa



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**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). and Young's modulus of 504 GPa. However, TM diborides are inherently hard but brittle, accompanied by crack formation during deformation [27]. Moreover, BN tends to form amorphous structures, as reported in sputtered Ti–B–N [28], Cr–B–N [29], and Zr–B–N [30] films. Combining the characteristics of TM–Si–N and TM–B–N films applied as protective coatings is essential. In this study, we fabricated ZrBSiTa and (ZrBSiTa)N<sub>x</sub> films through direct current (DC) magnetron cosputtering using ZrB<sub>2</sub>, Ta, and Si targets. The mechanical properties, thermal stability, and oxidation behavior of ZrBSiTa and (ZrBSiTa)N<sub>x</sub> films were investigated.

#### 2. Materials and Methods

ZrBSiTa and (ZrBSiTa)N<sub>x</sub> films were fabricated on silicon wafers through cosputtering. The cosputtering apparatus has been described in a previous study [31]. The target-substrate distance was 90 mm. The substrate holder, without heating, was rotated at 30 rpm. The DC powers applied to the ZrB<sub>2</sub> and Ta targets were fixed at 100 and 50 W, respectively, whereas the DC power on the Si target (P<sub>Si</sub>) varied from 0 to 50, 100, and 150 W. All the targets were 50.8 mm in diameter. The total flow rate of N<sub>2</sub> and Ar was 20 sccm, and the nitrogen flow ratio [R<sub>N2</sub> = N<sub>2</sub>/(N<sub>2</sub> + Ar)] was set at 0, 0.1, 0.2, and 0.4 for fabricating various batches of A, B, C, and D samples, respectively. The thermal stability test was performed at 800 and 900 °C for 10–30 min under purged Ar gas in a rapid thermal annealing (RTA, eRTP50, Giant-Tek, Miaoli, Taiwan) furnace with a ramping speed of 10 °C/s. Moreover, the oxidation behavior was evaluated after (ZrBSiTa)N<sub>x</sub> samples were annealed at 800 °C in the air for 0.5–12 h.

The chemical compositions of the ZrBSiTa and  $(ZrBSiTa)N_x$  films were analyzed using a field-emission electron probe microanalyzer (FE-EPMA, JXA-iHP200F, JEOL, Akishima, Japan) at a 12-kV accelerating voltage on the surface. The bonding characteristics of films were analyzed using an X-ray photoelectron spectroscope (XPS, PHI 5000 Versaprobe II, ULVAC–PHI, Kanagawa, Japan) with a monochromatic Al K<sub> $\alpha$ </sub> X-ray beam operated at 15 kV. The C 1s line from the carbon contamination on the free surface of a  $Zr_{10}B_9Ta_{18}N_{63}$ sample was 284.33 eV. The XPS spectra of Zr 3d, B 1s, Si 2p, Ta 4f, and N 1s core levels were recorded. The splitting energies were 2.43 and 1.91 eV for Zr 3d and Ta 4f doublets [32], respectively. The intensity ratios of  $I(3d_{5/2})$ : $I(3d_{3/2})$  and  $I(4f_{7/2})$ : $I(4f_{5/2})$  were set as 3:2 and 4:3 for the Zr and Ta doublets, respectively. An Ar<sup>+</sup> ion beam of 3 keV was used to sputter the films for depth profiling; the sputter etching rate was 8.2 nm/min for SiO<sub>2</sub>. XPS analyses were conducted at depths of 8.2, 16.4, 24.6, 32.8, 41.0, and 49.2 nm. The backgrounds were corrected via a Shirley function, and the peaks were fitted with a mixed Gaussian-Lorentzain function. The phases of the films were verified using X-ray diffraction (XRD; X'Pert PRO MPD, PANalytical, Almelo, The Netherlands) with Cu K<sub> $\alpha$ </sub> radiation using a grazing incidence technique at an incidence angle of 1°. The applied accelerating voltage and current of XRD were 45 kV and 40 mA, respectively. The nanostructures of the films with a protective C layer were observed using transmission electron microscopy (TEM, JEM-2010E, JEOL, Akishima, Japan). The mechanical properties of the films were measured using a nanoindentation tester (TI-900 Triboindenter, Hysitron, Minneapolis, MN, USA) equipped with a Berkovich diamond probe tip and calculated using the Oliver-Pharr method [33]. The indentation depth was 80 nm. The residual stress on the films was determined using the curvature method [34,35].

#### 3. Results

### 3.1. Chemical Compositions and Phase Structures of ZrBSiTa and (ZrBSiTa)N<sub>x</sub> Films

Table 1 lists the chemical compositions of as-deposited ZrBSiTa and (ZrBSiTa)N<sub>x</sub> films. The Si content revealed an increasing trend with increasing P<sub>Si</sub>. In contrast, the Zr, B, and Ta contents demonstrated a decreasing trend with increasing P<sub>Si</sub> for each batch sample, which implied that the sputtering yield of these sputter guns in the cosputtering apparatus was independent. The N content of batch B films decreased from 59.4 at.% to 54.5, 54.6, and 51.4 at.% as increasing P<sub>Si</sub> from 0 to 50, 100, and 150 W, whereas the N content of the

batch C and D samples remained constant at 61.4–64.6 and 63.0–63.5 at.%, respectively. For example, the batch D samples exhibited chemical compositions of  $Zr_{10}B_9Ta_{18}N_{63}$ ,  $Zr_7B_6Si_{10}Ta_{13}N_{64}$ ,  $Zr_5B_6Si_{17}Ta_9N_{63}$ , and  $Zr_4B_4Si_{21}Ta_8N_{63}$  when the applied  $P_{Si}$  was 0, 50, 100, and 150 W, respectively, which were accompanied by a deposition rate increasing from 4.7 to 5.7, 6.9, and 8.1 nm/min, respectively. The stoichiometric ratio (x) was higher than 1 for all the (ZrBSiTa)N<sub>x</sub> films. However, in a previous study [36], the value of x was less than 0.5 for (NbTaMoW)N<sub>x</sub> films, even for the sample fabricated under a high  $R_{N2}$  value of 0.4. This variation was attributed to the evident difference in affinity between N and the other elements. Mo2N and W2N are the preferentially formed Mo-N and W-N compounds during sputtering. The standard formation enthalpies for BN, TaN, ZrN, Si<sub>3</sub>N<sub>4</sub>, TaB<sub>2</sub>, and ZrB<sub>2</sub> at 298 K are -254.4, -252.3, -365.3, -744.8, -209.2, and -322.6 kJ/mol [37], respectively. N should preferentially bond to Zr and then bond to B, Ta, and Si, whereas B should preferentially bond to N, Zr, and Ta. Moreover, the ZrN, BN, and TaN had a stoichiometric ratio of 1, whereas the x value is 1.33 for  $Si_3N_4$ . Therefore, the x values were >1 for all the (ZrBSiTa)N<sub>x</sub> films.  $ZrB_{y}$ , as well as TiB<sub>y</sub> [38], tended to form overstoichiometric diboride thin films through sputtering [26]. In our previous study [39], a ZrB<sub>2.5</sub> (28.4% Zr-70.5% B-1.1% O) film was fabricated using a ZrB<sub>2</sub> target. However, all the ZrBSiTa and  $(ZrBSiTa)N_x$  films had understoichiometric B/Zr ratios of 0.9–1.6, which could be attributed to scattering and resputtering of light B atoms during cosputtering [26].

**Table 1.** Chemical compositions of ZrBSiTa and (ZrBSiTa)N<sub>x</sub> films.

	Power P <sub>Si</sub>		Chemical Composition (at.%)					
Sample	(W)	R <sub>N2</sub> <sup>a</sup>	Zr	В	Si	Ta	Ν	0
A1 Zr <sub>21</sub> B <sub>30</sub> Ta <sub>49</sub>	0	0	$20.9\pm0.4$	$29.3\pm0.3$	-	$48.6\pm0.7$	-	$1.2\pm0.9$
A2 Zr <sub>20</sub> B <sub>24</sub> Si <sub>13</sub> Ta <sub>43</sub>	50	0	$19.1\pm0.4$	$24.1\pm0.4$	$12.9\pm0.1$	$42.8\pm0.2$	-	$1.1\pm0.2$
A3 Zr <sub>18</sub> B <sub>29</sub> Si <sub>21</sub> Ta <sub>32</sub>	100	0	$17.7\pm0.1$	$28.8\pm0.3$	$20.7\pm0.2$	$31.0\pm0.4$	-	$1.8\pm0.1$
A4 Zr <sub>15</sub> B <sub>15</sub> Si <sub>42</sub> Ta <sub>28</sub>	150	0	$14.5\pm0.1$	$15.0\pm0.0$	$41.4\pm0.3$	$26.9\pm0.4$	-	$2.2\pm0.1$
B1 Zr <sub>10</sub> B <sub>11</sub> Ta <sub>19</sub> N <sub>60</sub>	0	0.1	$10.3\pm0.2$	$11.3\pm0.2$	-	$18.7\pm0.4$	$59.4\pm0.3$	$0.3\pm0.5$
B2 Zr <sub>9</sub> B <sub>11</sub> Si <sub>11</sub> Ta <sub>15</sub> N <sub>54</sub>	50	0.1	$8.7\pm0.1$	$10.9\pm0.0$	$10.6\pm0.1$	$14.8\pm0.3$	$54.5\pm0.4$	$0.5\pm0.6$
B3 Zr <sub>7</sub> B <sub>9</sub> Si <sub>17</sub> Ta <sub>12</sub> N <sub>55</sub>	100	0.1	$7.0\pm0.0$	$8.8\pm0.3$	$17.4\pm0.3$	$12.0\pm0.1$	$54.6\pm0.5$	$0.2\pm0.3$
B4 Zr <sub>6</sub> B <sub>9</sub> Si <sub>22</sub> Ta <sub>11</sub> N <sub>52</sub>	150	0.1	$6.4\pm0.0$	$8.4\pm0.3$	$22.1\pm0.4$	$11.3\pm0.2$	$51.4\pm0.5$	$0.4\pm0.1$
C1 Zr <sub>9</sub> B <sub>12</sub> Ta <sub>14</sub> N <sub>65</sub>	0	0.2	$8.8\pm0.1$	$11.9\pm0.4$	-	$14.3\pm0.4$	$64.6\pm0.9$	$0.4\pm0.4$
C2 Zr <sub>7</sub> B <sub>8</sub> Si <sub>9</sub> Ta <sub>12</sub> N <sub>64</sub>	50	0.2	$6.5\pm0.1$	$8.0\pm0.2$	$9.2\pm0.1$	$12.4\pm0.1$	$63.4\pm0.3$	$0.5\pm0.4$
C3 Zr <sub>5</sub> B <sub>7</sub> Si <sub>14</sub> Ta <sub>10</sub> N <sub>64</sub>	100	0.2	$5.1\pm0.1$	$6.7\pm0.1$	$14.3\pm0.2$	$9.6\pm0.1$	$64.0\pm0.2$	$0.3\pm0.4$
C4 Zr <sub>4</sub> B <sub>6</sub> Si <sub>20</sub> Ta <sub>8</sub> N <sub>62</sub>	150	0.2	$4.4\pm0.1$	$6.0\pm0.1$	$19.8\pm0.1$	$7.5\pm0.1$	$61.4\pm0.2$	$0.9\pm0.1$
D1 Zr <sub>10</sub> B <sub>9</sub> Ta <sub>18</sub> N <sub>63</sub>	0	0.4	$9.4\pm0.1$	9.1 ± 0.0	-	$18.2\pm0.1$	63.0 ± 0.3	$0.3\pm0.4$
D2 Zr <sub>7</sub> B <sub>6</sub> Si <sub>10</sub> Ta <sub>13</sub> N <sub>64</sub>	50	0.4	$6.8\pm0.0$	$6.2\pm0.2$	$10.3\pm0.1$	$13.0\pm0.2$	$63.5\pm0.1$	$0.2\pm0.3$
D3 Zr <sub>5</sub> B <sub>6</sub> Si <sub>17</sub> Ta <sub>9</sub> N <sub>63</sub>	100	0.4	$5.0\pm0.1$	$5.6\pm0.1$	$17.1\pm0.0$	$8.8\pm0.2$	$63.3\pm0.1$	$0.2\pm0.3$
$\begin{array}{c} D4\\ Zr_4B_4Si_{21}Ta_8N_{63}\end{array}$	150	0.4	$4.2\pm0.1$	$4.1\pm0.2$	$20.7\pm0.1$	$7.5\pm0.1$	$63.2\pm0.2$	$0.3\pm0.1$

<sup>a</sup> R<sub>N2</sub>: nitrogen flow ratio.

Table 2 lists the thicknesses and deposition rates of the fabricated ZrBSiTa and  $(ZrBSiTa)N_r$  films. The deposition rate increased with the increasing P<sub>Si</sub> level for all the films. The deposition rate decreased with increasing  $R_{N2}$ , which was attributed to the target poisoning effect [40] and the low sputtering efficiency of N correlated to that of Ar ions [41,42]. For example, the deposition rates for the  $Zr_{10}B_{11}Ta_{19}N_{60}$  (B1),  $Zr_9B_{12}Ta_{14}N_{65}$ (C1), and  $Zr_{10}B_9Ta_{18}N_{63}$  (D1) samples decreased from 10.7 to 6.6 and 4.7 nm/min as  $R_{N2}$ increased from 0.1 to 0.2 and 0.4. Figure 1 displays the GIXRD patterns of the as-fabricated ZrBSiTa and (ZrBSiTa)N<sub>x</sub> Films. The broad peaks observed at 2 $\theta$  of 36–38° for ZrBSiTa films and at 20 of 34° for (ZrBSiTa)N<sub>x</sub> films indicated that all the as-fabricated ZrBSiTa and  $(ZrBSiTa)N_x$  films formed amorphous structures. In our previous study [43], TaZrN films crystallized into a face-centered cubic phase and revealed a columnar structure. The addition of B and Si into TaZrN films affected the phase structures. Multicomponent alloys could form distinct structures (solid solution, intermediate phase, and bulk metallic glasses) depending on their atomic size difference ( $\delta$ ), mixing enthalpy ( $\Delta H_{mix}$ ), and mixing entropy ( $\Delta S_{mix}$ ) [44]. Multicomponent bulk metallic glasses have larger  $\delta$  (6%–18%) and more negative  $\Delta H_{mix}$  (-25–-37 kJ/mol) [44]. The batch A (ZrBSiTa) samples exhibited high  $\delta$  values of 24.0%, 22.6%, 24.2%, and 19.6%, significant and negative  $\Delta H_{mix}$  values of -48, -58, -65, and -66 kJ/mol, and medium mixing entropy values of 8.6, 10.7, 11.3, and 10.7 J/K.mol for  $Zr_{21}B_{30}Ta_{49}$  (A1),  $Zr_{20}B_{24}Si_{13}Ta_{43}$  (A2),  $Zr_{18}B_{29}Si_{21}Ta_{32}$  (A3), and Zr<sub>15</sub>B<sub>15</sub>Si<sub>42</sub>Ta<sub>28</sub> (A4), respectively, which resulted in forming amorphous structures. Moreover, sputtered BN [28,29] and SiN<sub>x</sub> films tended to be amorphous, which resulted in the formation of amorphous structures for the  $(ZrBSiTa)N_x$  films.

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Sample	Thickness (nm)	Deposition Time (min)	Deposition Rate (nm/min)
A1	815	120	6.8
A2	1073	120	8.9
A3	983	100	9.8
A4	881	80	11.0
B1	1608	150	10.7
B2	1530	120	12.8
B3	1684	120	14.0
B4	1536	90	17.1
C1	1189	180	6.6
C2	1593	180	8.8
C3	1377	120	11.5
C4	1547	120	12.9
D1	749	160	4.7
D2	1029	180	5.7

**Table 2.** Thicknesses and deposition rates of ZrBSiTa and (ZrBSiTa) $N_x$  films.

1167

1211

D3

D4

Figure 2 displays the XPS spectra and curve fitting of Zr 3d, B 1s, Si 2p, and Ta 4f for the batch A samples at a sputter depth of 49.2 nm. The XPS analysis results of batch A samples at sputter depths of 16.4–49.2 nm are listed in Table 3. The binding energies of Zr  $3d_{5/2}$  at 178.49–178.70 eV were recognized as Zr–B bonds in a ZrB<sub>2</sub> compound. The B 1s signals were determined at 187.01–187.33 eV, identified as B–Zr bonds. The reported Zr  $3d_{5/2}$  and B 1s binding energies for an epitaxial ZrB<sub>2</sub> film were 178.9 and 187.9 eV [45], respectively. The binding energy of Si–Si bonds was 98.43–98.77 eV. The binding energy of Ta  $4f_{7/2}$  for the Ta–Ta bonds was 21.88–22.08 eV, comparable to metallic Ta at 21.9 eV [32]. The Zr  $3d_{5/2}$  was also reported to be 178.8 eV in ZrSi<sub>2</sub> [46]. However, the standard formation enthalpy of ZrSi<sub>2</sub> at 298 K is -159.4 kJ/mol [32], which is lower than that of ZrB<sub>2</sub>. ZrSi<sub>2</sub> should be not the preferentially formed compound.

170

150

6.9

8.1



**Figure 1.** GIXRD patterns of the as-fabricated (**a**) ZrBSiTa and (ZrBSiTa) $N_x$  films prepared at  $R_{N2}$  of (**b**) 0.1, (**c**) 0.2, and (**d**) 0.4, respectively.

<b>Table 3.</b> XPS analysis results of batch A films at sputter depths of 16.4–49.2 nm.	
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Sample	Zr 3d <sub>5/2</sub> (eV)	B 1s (eV)	Si 2p (eV)	Ta 4f <sub>7/2</sub> (eV)
A1	$178.52\pm0.01$	$187.02\pm0.02$	_	$21.93\pm0.02$
A2	$178.49\pm0.04$	$187.01\pm0.04$	$98.43 \pm 0.02$	$21.88\pm0.04$
A3	$178.68\pm0.07$	$187.23\pm0.06$	$98.75\pm0.16$	$22.03\pm0.04$
A4	$178.70\pm0.06$	$187.33\pm0.03$	$98.77\pm0.06$	$22.08\pm0.02$

Figure 3 displays the XPS spectra of Zr 3d, B 1s, Si 2p, Ta 4f, and N 1s core levels for batch D films at a depth of 49.2 nm. Table 4 lists the XPS analysis results of the batch D samples at sputter depths of 16.4–49.2 nm. Figure 3a shows the curve fitting of the Zr profiles, which were split into two 3d doublets, representing Zr–N bonds for ZrN and Zr<sub>3</sub>N<sub>4</sub> components. The average Zr  $3d_{5/2}$  values at sputter depths of 16.4–49.2 nm were 179.60–180.52 and 180.84–181.46 eV, respectively. The B 1s signals of 189.74–190.44 eV were identified as B–N bonds comparable with reported values of 190.3 eV [28,47]. The Si signals of the Zr<sub>7</sub>B<sub>6</sub>Si<sub>10</sub>Ta<sub>13</sub>N<sub>64</sub>, Zr<sub>5</sub>B<sub>6</sub>Si<sub>17</sub>Ta<sub>9</sub>N<sub>63</sub>, and Zr<sub>4</sub>B<sub>4</sub>Si<sub>21</sub>Ta<sub>8</sub>N<sub>63</sub> films comprised two components whose binding energies were 99.02–99.34 and 101.15–101.28 eV for the Si–Si and Si–N bonds, respectively. Previous studies [32,48,49] have reported Si 2p signals at 99.2, 101.80, 102.60, and 103–103.50 eV to be Si–Si, Si–N, Si–N–O, and Si–O bonds, respectively. Therefore, only Si–N and Si–Si bonds were detected for the batch D films. Figure 3d shows the Ta signals, split into two 4f doublets, representing Ta–N bonds for TaN and Ta<sub>3</sub>N<sub>5</sub>. The Ta  $4f_{7/2}$  signals were determined at 22.56–22.95 and 23.89–24.38 eV for TaN and Ta<sub>3</sub>N<sub>5</sub>, respectively, which were comparable with reported 22.2–23.0 [50,51] and 24.2 [52] eV. All the aforementioned binding energies of the  $Zr_{10}B_9Ta_{18}N_{63}$  (D1) sample were lower than those of the  $Zr_7B_6Si_{10}Ta_{13}N_{64}$ ,  $Zr_5B_6Si_{17}Ta_9N_{63}$ , and  $Zr_4B_4Si_{21}Ta_8N_{63}$  samples, which could be attributed to a charge effect for the Si-containing films with high resistivity.

Table 4. XPS analysis results of batch D films at sputter depths of 16.4–49.2 nm.

Sample	Zr 3d <sub>5/2</sub> (eV)		B 1s (eV)	Si 2p (eV)		Ta 4f <sub>7/2</sub> (eV)	
	(ZrN)	(Zr <sub>3</sub> N <sub>4</sub> )		(Si)	(Si <sub>3</sub> N <sub>4</sub> )	(TaN)	(Ta <sub>3</sub> N <sub>5</sub> )
D1	$179.60\pm0.02$	$180.84\pm0.03$	$189.74\pm0.04$	_	_	$22.56\pm0.02$	$23.89\pm0.03$
D2	$180.06\pm0.02$	$181.12\pm0.02$	$190.26\pm0.04$	$99.02\pm0.05$	$101.15\pm0.05$	$22.95\pm0.02$	$24.34\pm0.03$
D3	$180.52\pm0.05$	$181.46\pm0.03$	$190.44\pm0.04$	$99.34 \pm 0.05$	$101.28\pm0.05$	$22.91\pm0.04$	$24.35\pm0.01$
D4	$180.42\pm0.02$	$181.46\pm0.02$	$190.42\pm0.06$	$99.25\pm0.07$	$101.28\pm0.05$	$22.95\pm0.03$	$24.38\pm0.02$



**Figure 2.** XPS patterns of (a) Zr 3d and B 1s, (b) Si 2p, and (c) Ta 4f signals of the as-deposited A1 ( $Zr_{21}B_{30}Ta_{49}$ ), A2 ( $Zr_{20}B_{24}Si_{13}Ta_{43}$ ), A3 ( $Zr_{18}B_{29}Si_{21}Ta_{32}$ ), and A4 ( $Zr_{15}B_{15}Si_{42}Ta_{28}$ ) samples at a sputter depth of 49.2 nm.



Figure 3. XPS patterns of (a) Zr 3d, (b) B 1s, (c) Si 2p, (d)Ta 4f, and (e) N 1s signals of the as-deposited D1 ( $Zr_{10}B_9Ta_{18}N_{63}$ ), D2 ( $Zr_7B_6Si_{10}Ta_{13}N_{64}$ ), D3 ( $Zr_5B_6Si_{17}Ta_9N_{63}$ ), and D4 ( $Zr_4B_4Si_{21}Ta_8N_{63}$ ) samples at a depth of 49.2 nm.

# 3.2. Mechanical Properties

Table 5 lists the mechanical properties of the ZrBSiTa and (ZrBSiTa)N<sub>x</sub> films. The ZrBSiTa films with a Si content of 0–21 at.% maintained a hardness (*H*) of 18.4–19.1 GPa, elastic modulus (*E*) of 256–264 GPa, and elastic recovery ( $W_e$ ) of 31%–34%, whereas the A4

sample with a high Si content of 42 at.% exhibited a lower H value of 14.3 GPa, E value of 242 GPa, and  $W_e$  value of 18%. Adding N into the ZrBSiTa matrix did not enhance the mechanical properties. For most transition metal nitride with crystalline structures, their mechanical properties were higher than corresponding metallic films due to the variation in bonding structures. SiN $_x$  and BN tended to form amorphous structures fabricated through sputtering processes; therefore, the  $(ZrBSiTa)N_x$  films exhibited amorphous structures and had low mechanical properties. The increase in Si content of the (ZrBSiTa)N<sub>x</sub> films increased the mechanical properties, which were accompanied by increased residual stresses. For example, the H of batch C samples increased from 11.0 to 12.3, 14.0, and 15.0 GPa as the compressive residual stress increased from 0.61 to 0.81, 0.87, and 1.09 GPa. Residual stress was recognized as a minor effect on the mechanical properties of crystalline films, in which crystalline size and phase structure were the major factors. In contrast, residual stress dominated the mechanical properties of amorphous films. Figure 4 exhibits the relationship between H and residual stress of the ZrBSiTa and (ZrBSiTa)N<sub>x</sub> films. Linear fitting lines for each batch sample are shown in this figure. The hardness values decreased with the increasing N content in the films. The batches C and D samples exhibited a similar N content of 62-65 at.%, and their hardness-stress fitting lines were almost overlapped.

**Table 5.** Mechanical properties of ZrBSiTa and (ZrBSiTa) $N_x$  films.

Sample	H <sup>a</sup> (GPa)	E <sup>b</sup> (GPa)	H/E	H <sup>3</sup> /E <sup>2</sup> (GPa)	W <sub>e</sub> <sup>c</sup> (%)	$\sigma$ <sup>d</sup> (GPa)
A1	$18.5\pm0.2$	$256\pm3$	0.072	0.096	32	$-0.80\pm0.15$
A2	$19.1\pm0.3$	$264\pm7$	0.072	0.099	34	$-0.84\pm0.01$
A3	$18.4\pm0.3$	$261\pm4$	0.071	0.092	31	$-0.54\pm0.08$
A4	$14.3\pm0.2$	$242\pm5$	0.059	0.050	18	$-0.26\pm0.05$
B1	$13.0\pm0.1$	$215\pm 6$	0.061	0.048	44	$-0.45\pm0.05$
B2	$14.5\pm0.2$	$221\pm5$	0.066	0.063	47	$-0.60\pm0.03$
B3	$14.9\pm0.1$	$223\pm2$	0.067	0.067	49	$-0.75\pm0.23$
B4	$14.9\pm0.3$	$221\pm4$	0.067	0.068	52	$-0.84\pm0.05$
C1	$11.0\pm0.1$	$181\pm5$	0.061	0.041	43	$-0.61\pm0.12$
C2	$12.3\pm0.3$	$187\pm4$	0.066	0.054	46	$-0.81\pm0.08$
C3	$14.0\pm0.2$	$195\pm3$	0.072	0.072	49	$-0.87\pm0.16$
C4	$15.0\pm0.2$	$197\pm3$	0.076	0.087	52	$-1.09\pm0.10$
D1	$11.5\pm0.5$	$207\pm 6$	0.056	0.035	15	$-0.64\pm0.03$
D2	$12.3\pm0.4$	$213\pm4$	0.058	0.041	19	$-0.77\pm0.01$
D3	$13.5\pm0.2$	$219\pm 6$	0.062	0.051	23	$-0.92\pm0.08$
D4	$14.1\pm0.3$	$218\pm5$	0.065	0.058	25	$-0.90\pm0.12$

<sup>a</sup> *H*: hardness. <sup>b</sup> *E*: elastic modulus. <sup>c</sup>  $W_e$ : elastic recovery. <sup>d</sup>  $\sigma$ : residual stress.



Figure 4. Relationship between hardness and residual stress of ZrBSiTa and (ZrBSiTa)N<sub>x</sub> films.

# 3.3. Thermal Stability of ZrBSiTa and ZrBSiTaN Films

The thermal stability tests were performed at 800 and 900 °C within purged Ar gas in an RTA furnace. Figure 5 shows the GIXRD patterns of the ZrBSiTa films after 10 min annealing at 800 °C, which exhibits the formation of tetragonal  $ZrO_2$  (t-ZrO<sub>2</sub>) (ICDD 00-042-1164); monoclinic ZrO<sub>2</sub> (*m*-ZrO<sub>2</sub>) (ICDD 00-037-1484); and orthorhombic  $Ta_2O_5$  (ICDD 00-025-0922) phases for the annealed  $Zr_{21}B_{30}Ta_{49}$  (A1),  $Zr_{20}B_{24}Si_{13}Ta_{43}$  (A2), and Zr<sub>18</sub>B<sub>29</sub>Si<sub>21</sub>Ta<sub>32</sub> (A3) films. A TaSi<sub>2</sub> (ICDD 00-038-0483) phase was observed for the annealed  $Zr_{15}B_{15}Si_{42}Ta_{28}$  (A4) film with a high Si content. The O originated from the residual contamination in the chamber. The SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> which was possibly present should be amorphous and not shown in these XRD patterns. The aforementioned four ZrBSiTa films were annealed at the same time, which implied that  $Zr_{15}B_{15}Si_{42}Ta_{28}$  had higher oxidation resistance among the ZrBSiTa films. In contrast, all the (ZrBSiTa)N<sub>x</sub> films maintained an amorphous phase in their GIXRD patterns after 10 min annealing at 800 °C. After extending the annealing time to 20 and 30 min, all the (ZrBSiTa)N<sub>x</sub> films were amorphous except for the  $Zr_9B_{12}Ta_{14}N_{65}$  (C1) and  $Zr_{10}B_9Ta_{18}N_{63}$  (D1) films. The C1 and D1 samples exhibited ZrO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub> phases after 30 and 20 min annealing, respectively. Table 6 lists the XRD analysis results of the ZrBSiTa and  $(ZrBSiTa)N_x$  films annealed at 800 and 900 °C in Ar gas.



**Figure 5.** GIXRD patterns of ZrBSiTa films,  $Zr_{21}B_{30}Ta_{49}$  (A1),  $Zr_{20}B_{24}Si_{13}Ta_{43}$  (A2),  $Zr_{18}B_{29}Si_{21}Ta_{32}$  (A3), and  $Zr_{15}B_{15}Si_{42}Ta_{28}$  (A4), after annealing in Ar at 800 °C for 10 min.

The oxidation and crystallization of the  $Zr_{10}B_{11}Ta_{19}N_{60}$  (B1) and  $Zr_9B_{11}Si_{11}Ta_{15}N_{54}$  (B2) films occurred after 10 min annealing at 900 °C. In contrast, crystallization reflections became evident for the  $Zr_7B_9Si_{17}Ta_{12}N_{55}$  (B3) films after 20 min annealing, and the  $Zr_6B_9Si_{22}Ta_{11}N_{52}$  (B4) films maintained an amorphous phase after annealing for up to 30 min, as Figure 6a shows. The oxide phases of the (ZrBSiTa)N<sub>x</sub> films comprised *m*-ZrO<sub>2</sub>, *t*-ZrO<sub>2</sub>, and Ta<sub>2</sub>O<sub>5</sub>. The oxidation and crystallization of the  $Zr_9B_{12}Ta_{14}N_{65}$  (C1) and  $Zr_7B_8Si_9Ta_{12}N_{64}$  (C2) films occurred after 10 min annealing at 900 °C. In contrast, crystallization reflections became evident for the  $Zr_5B_7Si_{14}Ta_{10}N_{64}$  (C3) films after 30 min annealing, and the  $Zr_4B_6Si_{20}Ta_8N_{62}$  (C4) films maintained an amorphous phase after annealing for up to 30 min. The oxidation and crystallization of the  $Zr_{10}B_9Ta_{18}N_{63}$  (D1) films occurred after 10 min annealing at 900 °C, whereas the  $Zr_7B_6Si_{10}Ta_{13}N_{64}$  (D2),  $Zr_5B_6Si_{17}Ta_9N_{63}$  (D3), and  $Zr_4B_4Si_{21}Ta_8N_{63}$  (D4) films maintained an amorphous phase after annealing for up to 30 min. Figure 6b,c display the GIXRD patterns of the 900 °C and 30 min annealed batches C and D samples, respectively.



**Figure 6.** GIXRD patterns of (**a**) batch B, (**b**) batch C, and (**c**) batch D films after annealing in Ar at 900 °C for 30 min.

<b>Table 6.</b> Phases of the ZrBSiTa and (ZrBSiTa)N $_x$ films annealed at 800 and 900 °C in Ar ga	ıs.

Sample	Annealing Time (min)					
	10	20	30			
annealed at 800 °C						
A1, A2, A3	$ZrO_2^a + Ta_2O_5$	—	—			
A4	TaSi <sub>2</sub>	—	—			
B1, B2, B3, B4	amorphous	amorphous	amorphous			
C1	amorphous	amorphous	$ZrO_2 + Ta_2O_5$			
C2, C3, C4	amorphous	amorphous	amorphous			
D1	amorphous	$ZrO_2 + Ta_2O_5$	-			
D2, D3, D4	amorphous	amorphous	amorphous			
	annealed	at 900 °C				
B1, B2	$ZrO_2 + Ta_2O_5$	$ZrO_2 + Ta_2O_5$	$ZrO_2 + Ta_2O_5$			
B3	amorphous	$ZrO_2 + Ta_2O_5$	$ZrO_2 + Ta_2O_5$			
B4	amorphous	amorphous	amorphous			
C1, C2	$ZrO_2 + Ta_2O_5$	$ZrO_2 + Ta_2O_5$	$ZrO_2 + Ta_2O_5$			
C3	amorphous	$ZrO_2 + Ta_2O_5$	$ZrO_2 + Ta_2O_5$			
C4	amorphous	amorphous	amorphous			
D1	$ZrO_2 + Ta_2O_5$	$ZrO_2 + Ta_2O_5$	$ZrO_2 + Ta_2O_5$			
D2, D3, D4	amorphous	amorphous	amorphous			
$a 7r \cap f + 7r \cap f + m - 7r \cap f$						

<sup>a</sup>  $ZrO_2$ : t- $ZrO_2 + m$ - $ZrO_2$ .

Figure 7a shows a cross-sectional TEM (XTEM) image of the  $Zr_{10}B_9Ta_{18}N_{63}$  (D1) film after 30 min annealing at 900 °C in Ar. The  $Zr_{10}B_9Ta_{18}N_{63}$  film detached from the Si substrate after annealing. The original  $Zr_{10}B_9Ta_{18}N_{63}$  film/Si substrate interface exposed the underlying carbon film on the TEM sample holder. Figure 7b displays the selected area electron diffraction (SAED) pattern of the annealed  $Zr_{10}B_9Ta_{18}N_{63}$  sample revealing ring patterns of the Ta<sub>2</sub>O<sub>5</sub>, *m*-ZrO<sub>2</sub>, and *t*-ZrO<sub>2</sub> phases. Figure 7c displays a high-resolution TEM (HRTEM) image of the annealed  $Zr_{10}B_9Ta_{18}N_{63}$  film, which depicts lattice fringes correlating to *d*-spacing values of 0.308, 0.389, 0.364, and 0.283 nm for Ta<sub>2</sub>O<sub>5</sub> (200), Ta<sub>2</sub>O<sub>5</sub> (001), *m*-ZrO<sub>2</sub> (011), and *m*-ZrO<sub>2</sub> (111) planes, respectively. The lattice fringes with a *d*spacing of 0.315 nm could represent either Ta<sub>2</sub>O<sub>5</sub> (1 11 0) or *m*-ZrO<sub>2</sub> (-111) planes. Figure 8a shows the XTEM image of the  $Zr_4B_4Si_{21}Ta_8N_{63}$  (D4) film after 30 min annealing at 900 °C in Ar. The  $Zr_4B_4Si_{21}Ta_8N_{63}$  film was detached from the Si substrate. Figure 8b shows an amorphous SAED pattern. The HRTEM image observes no crystalline lattice fringes (Figure 8c). The  $Zr_4B_4Si_{21}Ta_8N_{63}$  film maintained an amorphous phase for up to 30 min as annealed at 900 °C.



**Figure 7.** (a) XTEM image and (b) SAED pattern of the  $Zr_{10}B_9Ta_{18}N_{63}$  film after 30 min annealing at 900 °C in Ar, (c) HRTEM image of the area shown in (a).



**Figure 8.** (a) XTEM image and (b) SAED pattern of the  $Zr_4B_4Si_{21}Ta_8N_{63}$  film after 30 min annealing at 900 °C in Ar, (c) HRTEM image of the area shown in (a).

## 3.4. Oxidation Behavior of (ZrBSiTa)N<sub>x</sub> Films

The (ZrBSiTa)N<sub>x</sub> samples were annealed at 800  $^{\circ}$ C in air for 0.5, 1, 2, and 12 h. Figure 9 shows the GIXRD patterns of the batch B films after annealing at 800 °C in air. The *t*-ZrO<sub>2</sub>, m-ZrO<sub>2</sub>, and Ta<sub>2</sub>O<sub>5</sub> phases formed for the annealed Zr<sub>10</sub>B<sub>11</sub>Ta<sub>19</sub>N<sub>60</sub> (B1) sample, whereas the  $Zr_9B_{11}Si_{11}Ta_{15}N_{54}$  (B2),  $Zr_7B_9Si_{17}Ta_{12}N_{55}$  (B3), and  $Zr_6B_9Si_{22}Ta_{11}N_{52}$  (B4) samples maintained an amorphous phase after annealing for 0.5 h. The one h annealed samples revealed XRD patterns similar to those of the 0.5 h annealed samples. After 2 h annealing, the  $Zr_9B_{11}Si_{11}Ta_{15}N_{54}$  sample crystallized, and the  $Zr_7B_9Si_{17}Ta_{12}N_{55}$  and  $Zr_6B_9Si_{22}Ta_{11}N_{52}$ samples maintained an amorphous phase. The Zr<sub>7</sub>B<sub>9</sub>Si<sub>17</sub>Ta<sub>12</sub>N<sub>55</sub> and Zr<sub>6</sub>B<sub>9</sub>Si<sub>22</sub>Ta<sub>11</sub>N<sub>52</sub> samples crystallized after 12 h annealing. The oxidation behavior of batches C and D samples was similar to those of the batch B samples. The Si content affected the oxidation resistance of  $(ZrBSiTa)N_x$  films. The B1, C1, and D1 samples without Si content oxidized after 0.5 h annealing at 800 °C, whereas the B2, C2, and D2 samples with Si contents of 9-11 at.% oxidized after 2 h annealing. The B3, C3, D3, B4, C4, and D4 samples with Si contents of 14–22 at.% maintained an amorphous phase after 2 h annealing. In this study, B and Si in the (ZrBSiTa) $N_x$  films stabilized the amorphous phase. However, the oxidation resistance of  $(ZrBSiTa)N_x$  films was determined by the amorphous Si<sub>3</sub>N<sub>4</sub> content, which was comparable with the oxidation behavior of ZrSiN films with a high Si content (≥25 at.%) [16].



**Figure 9.** GIXRD patterns of the batch B films,  $Zr_{10}B_{11}Ta_{19}N_{60}$  (B1),  $Zr_9B_{11}Si_{11}Ta_{15}N_{54}$  (B2),  $Zr_7B_9Si_{17}Ta_{12}N_{55}$  (B3), and  $Zr_6B_9Si_{22}Ta_{11}N_{52}$  (B4), after annealing at 800 °C in the air for (**a**) 0.5, (**b**) 1, (**c**) 2, and (**d**) 12 h.

Figure 10a depicts an XTEM image of the  $Zr_4B_4Si_{21}Ta_8N_{63}$  (D4) film after 12 h annealing at 800 °C in the air. An oxide scale of 531 nm (zone A) was observed, and the SAED pattern (Figure 10b) indicated that this scale was crystalline and consisted of *t*-ZrO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub> phases. Beneath the oxide scale, zone B of the annealed  $Zr_4B_4Si_{21}Ta_8N_{63}$  film exhibited a dense structure, and its SAED pattern showed an amorphous phase (Figure 10c). Figure 10d shows an HRTEM image of the surface oxide scale, and lattice fringes identified for tetragonal ZrO<sub>2</sub> (101) and orthorhombic Ta<sub>2</sub>O<sub>5</sub> (001) planes are indicated. Figure 10e depicts the EDS analysis of the annealed  $Zr_4B_4Si_{21}Ta_8N_{63}$  film, which suggests that the  $Zr_4B_4Si_{21}Ta_8N_{63}$  film is partially oxidized. Zone A was oxide-dominant, and zone B was amorphous nitride-dominant after 12 h annealing at 800 °C in the air.



**Figure 10.** (a) XTEM image, (b) and (c) SAED patterns, and (e) EDS analysis of the  $Zr_4B_4Si_{21}Ta_8N_{63}$  film after 12 h annealing at 800 °C in the air, (d) HRTEM image of the area shown in (a).

Figure 11a displays an XTEM image of the  $Zr_4B_4Si_{21}Ta_8N_{63}$  film after 24 h annealing at 800 °C in the air. The oxide scale (zone A) expanded relative to that of the 12 h annealed  $Zr_4B_4Si_{21}Ta_8N_{63}$  film. The SAED patterns of regions I, II, and III indicated in Figure 11a are shown in Figure 11b–d, respectively. Region I, the outermost part of the oxide scale, exhibits diffraction rings of *m*-ZrO<sub>2</sub>, *t*-ZrO<sub>2</sub>, and Ta<sub>2</sub>O<sub>5</sub> phases. In contrast, the inner part of the oxide scale (Region II) and the unoxidized film (Region III) are amorphous. Figure 11e shows an HRTEM image of region I displaying crystalline lattice fringes. Figure 11f displays the EDS analysis results of the 24 h annealed  $Zr_4B_4Si_{21}Ta_8N_{63}$  sample.



**Figure 11.** (a) XTEM image, (b–d) SAED patterns, and (f) EDS analysis of the  $Zr_4B_4Si_{21}Ta_8N_{63}$  film after 24 h annealing at 800 °C in the air, (e) HRTEM image of the area shown in (a).

### 4. Conclusions

This study fabricated ZrBSiTa and (ZrBSiTa) $N_x$  films through cosputtering. The main findings of this study are as follows:

- (1) All the as-fabricated ZrBSiTa and (ZrBSiTa) $N_x$  films exhibited amorphous structures due to incorporating B and Si. The overstoichiometric ratio (x > 1) was obtained for the (ZrBSiTa) $N_x$  films.
- (2) The as-fabricated ZrBSiTa films exhibited hardness values of 14.3-19.1 GPa and Young's modulus values of 242-264 GPa. The hardness and Young's modulus values of the (ZrBSiTa)N<sub>x</sub> thin films decreased to 11.0-15.0 and 181-223 GPa, respectively.

- (3) The amorphous (ZrBSiTa)N<sub>x</sub> films with high Si contents exhibited high thermal stability when annealed at 800 and 900 °C for up to 30 min in an Ar-purged atmosphere.
- (4) The Si content dominated the oxidation resistance of  $(ZrBSiTa)N_x$  films. The  $(ZrBSiTa)N_x$  films with Si contents of 14–22 at.% maintained an amorphous phase after 2 h annealing at 800 °C in air. The lower part of the  $Zr_4B_4Si_{21}Ta_8N_{63}$  film held amorphous nitride after extending the annealing time to 24 h.

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