

Article

Effects of Nitrogen Flow Ratio on Structures, Bonding Characteristics, and Mechanical Properties of ZrN_x Films

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Abstract: ZrN_x ($x = 0.67\text{--}1.38$) films were fabricated through direct current magnetron sputtering by a varying nitrogen flow ratio [$N_2/(Ar + N_2)$] ranging from 0.4 to 1.0. The structural variation, bonding characteristics, and mechanical properties of the ZrN_x films were investigated. The results indicated that the structure of the films prepared using a nitrogen flow ratio of 0.4 exhibited a crystalline cubic ZrN phase. The phase gradually changed to a mixture of crystalline ZrN and orthorhombic Zr_3N_4 followed by a Zr_3N_4 dominant phase as the N_2 flow ratio increased up to >0.5 and >0.85 , respectively. The bonding characteristics of the ZrN_x films comprising Zr–N bonds of ZrN and Zr_3N_4 compounds were examined by X-ray photoelectron spectroscopy and were well correlated with the structural variation. With the formation of orthorhombic Zr_3N_4 , the nanoindentation hardness and Young's modulus levels of the ZrN_x ($x = 0.92\text{--}1.38$) films exhibited insignificant variations ranging from 18.3 to 19.0 GPa and from 210 to 234 GPa, respectively.

Keywords: bonding characteristics; mechanical properties; sputtering

1. Introduction

Multifunctional ZrN films have been extensively investigated due to their characteristics including golden yellow appearance [1–3], high hardness [3–6], corrosion resistance [7–9], and wear resistance [10]. The nitrogen flow rate in reactive sputtering affects the structure and composition of fabricated MeN_x ($Me = Ti, Zr, Hf$) films [11–13], which varied the characteristics of these films. The B1 structure is a familiar structure for transition metal nitrides, in which N occupies the interstitial sites of close-packed metal atoms. Moreover, a wide composition range, with point defects in the B1 structure, was obtained for transition metal nitrides [14]. By contrast, N-rich compounds such as Ti_3N_4 , Zr_3N_4 , and Hf_3N_4 have been reported [15]. Zr_3N_4 crystallizes in an orthorhombic (o- Zr_3N_4) [16–18] or cubic (c- Zr_3N_4) [19–23] phase. o- Zr_3N_4 was reported as a transparent insulator [16,24], whereas c- Zr_3N_4 with a cubic Th_3P_4 -type structure was suggested as an alternating hard material [19,23]. Mattesini et al., [23] reported the calculated hardness level of c- Zr_3N_4 to be 17.5–19.7 GPa. Chhowalla and Unalan [25] announced that the filtered cathodic arc fabricated c- Zr_3N_4 films stabilized by a high residual stress and showed a high hardness of 36 GPa, compared to 27 GPa for the low-stressed o- Zr_3N_4 films. Zr_3N_4 contained films fabricated through sputtering technologies that were also reported either in the o- Zr_3N_4 or the c- Zr_3N_4 forms [12,16,18,26,27]. Previous studies [12,16,28] have reported that interstitial N is incorporated into the ZrN structure to form a Zr_3N_4 phase as the nitrogen flow ratio was higher than the critical level to form stoichiometric ZrN . Takeyama et al., [18] reported that a bilayered $ZrN/o-Zr_3N_4$ barrier was thermally stable undergoing the annealing at 500 °C for 60 min, but the o- Zr_3N_4 barrier was metastable in the Zr–N system. Kroll [15] proposed that c- Zr_3N_4 is

obtained in a high-pressure state. Alternatively, Meng et al., [27] reported the phase transformation from ZrN to c-Zr₃N₄ under high-compressive stress by increasing the substrate bias voltage in direct current magnetron sputtering (DCMS). In a previous study [29], HfN_x films with stoichiometric variable x in the range of 0.81–2.07 were deposited through DCMS using nitrogen flow ratios of 0.1 to 1.0. The structure varied from a δ -HfN phase to a near-amorphous structure as the stoichiometric variable x increased, which was accompanied by a change in the bonding characteristics from HfN to Hf₃N₄-dominant and a decrease in mechanical properties. In this study, the influences of nitrogen flow ratio on the structural evolution, bonding characteristics, and mechanical properties of ZrN_x films fabricated through DCMS were investigated.

2. Materials and Methods

ZrN_x films were prepared on silicon substrates through reactive DCMS. Figure 1 schematically displays the related positions of sputter targets and the samples in the sputtering chamber. A sputtering gun (gun 1) with Zr target was operated at 150 W in the sputtering process using a N₂ flow ratio [$f = N_2 / (Ar + N_2)$] ranging from 0.50 to 0.85 and a sputter time of 180 min. As the deposition rate decreased with increasing N₂ flow ratios (Table 1), both guns 1 and 2, with powers of 150 W, were utilized for raising the deposition rate of the process with $f = 1.00$. Zr₆₀N₄₀ films prepared with an N₂ flow ratio of 0.4, gun 1 power of 300 W, and sputter time of 60 min, that were reported in a previous study [30], are discussed for comparison. The diameter of Zr targets was 50.8 mm. The total flow rates of Ar and N₂ were fixed at 20 sccm with a working pressure of 0.4 Pa. The target-to-substrate distance was 90 mm. The electrically-grounded substrate holder was rotated at 5 rpm.

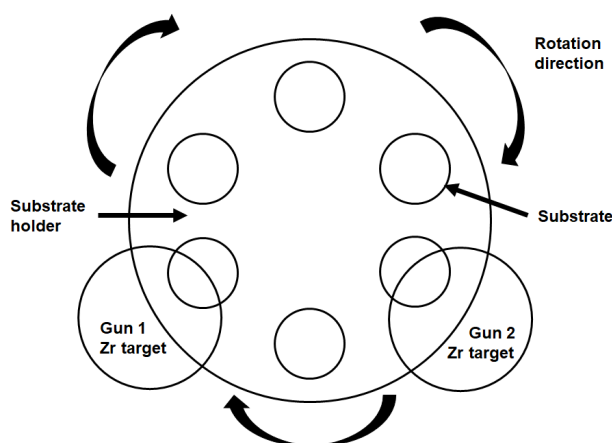


Figure 1. Relationship of sputter targets to the sample positions.

Table 1. Chemical composition and deposition rates of ZrN_x films prepared using various N₂ flow ratios.

Sample	f^a	Chemical Composition (at.%)				x^b	Thickness (nm)	D ^c (nm/min)
		Zr	N	Si	O			
P₁^d = 300 W, P₂^e = 0 W								
Zr ₆₀ N ₄₀	0.40	57.9 ± 0.8	38.8 ± 0.8	-	3.3 ± 0.1	0.67	820	13.7
P₁ = 150 W, P₂ = 0 W								
Zr ₅₂ N ₄₈	0.50	49.3 ± 0.8	46.4 ± 1.1	1.6 ± 0.0	2.5 ± 0.2	0.92	680	3.8
Zr ₅₀ N ₅₀	0.65	48.0 ± 2.0	47.3 ± 2.2	1.8 ± 0.0	2.8 ± 0.3	1.00	616	3.4
Zr ₄₈ N ₅₂	0.75	44.1 ± 0.4	47.8 ± 0.3	4.8 ± 0.1	3.2 ± 0.1	1.08	556	3.1
Zr ₄₅ N ₅₅	0.85	39.5 ± 1.6	47.5 ± 2.2	10.8 ± 0.4	2.2 ± 0.2	1.22	348	1.9
P₁ = 150 W, P₂ = 150 W								
Zr ₄₂ N ₅₈	1.00	40.5 ± 0.0	56.0 ± 0.2	1.5 ± 0.2	2.0 ± 0.1	1.38	694	3.9

^a f : N₂ flow ratio; ^b x : stoichiometric variable; ^c D: deposition rate; ^d P₁: power on gun 1; ^e P₂: power on gun 2.

A field-emission electron probe microanalyzer (FE-EPMA, JXA-8500F, JEOL, Akishima, Japan) was used to analyze the chemical composition of the films. The thickness of films was evaluated by field emission scanning electron microscopy (FE-SEM, S4800, Hitachi, Tokyo, Japan). An X-ray diffractometer (XRD, X'Pert PRO MPD, PANalytical, Almelo, The Netherlands) with Cu K α radiation was used to analyze the phases of the films, using the grazing incidence technique with an incidence angle of 1°. The hardness and Young's modulus values of films were measured using a nanoindentation tester (TI-900 Triboindenter, Hysitron, MN, USA) equipped with a Berkovich diamond probe tip, and were determined from 8 measurements based on the Oliver and Pharr method [31]. The indentation depth was 50 nm. The residual stress of the films measured by the curvature method was calculated using Stoney's equation [32,33],

$$\sigma_f t_f = \frac{E_s h_s^2}{6(1-\nu_s)R_f} \quad (1)$$

where σ_f is the residual stress, t_f is the film thickness, E_s is the Young's modulus of Si (130.2 GPa), ν_s is Poisson's ratio for Si (0.279), h_s is the substrate thickness (525 μm), and R_f is the radius of the curvature of the sample. The chemical states of the constituent elements were examined by using an X-ray photoelectron spectroscope (XPS, PHI 1600, PHI, Kanagawa, Japan) with an Mg K α X-ray beam and calibrated with the C 1s line at 284.6 eV. The nanostructure of the samples with a protective Pt layer was observed using transmission electron microscopy (TEM, JEM-2010F, JEOL, Akishima, Japan). The average surface roughness (R_a) of the films determined from 3 measurements was evaluated by using an atomic force microscope (AFM, Dimension 3100 SPM, NanoScope IIIa, Veeco, Santa Barbara, CA, USA) with a scanned area of 5 $\mu\text{m} \times 5 \mu\text{m}$ [33].

3. Results

3.1. Chemical Compositions and Crystalline Phases

Table 1 lists the chemical composition of the ZrN $_x$ films fabricated with various f values. The ZrN $_x$ samples were named in the form Zr $_y$ N $_{(100-y)}(f)$. The silicon contents were 1.5–1.8 at.% for the Zr $_{52}$ N $_{48}$ (0.50), Zr $_{50}$ N $_{50}$ (0.65), and Zr $_{42}$ N $_{58}$ (1.00) films with thicknesses of 616 to 694 nm, whereas the Zr $_{48}$ N $_{52}$ (0.75) and Zr $_{45}$ N $_{55}$ (0.85) films exhibited high Si contents of 4.8 and 10.8 at.%, respectively, which were attributed to lower thickness values of 556 and 348 nm. Therefore, the Si signals contributed by the Si substrates were observed. In our previous study [30], the Zr $_{60}$ N $_{40}$ (0.40) films prepared using the same sputter equipment with a sputter power of 300 W, N $_2$ flow ratio of 0.4, and sputter time of 60 min exhibited a thickness of 820 nm and Si-free chemical composition. The O contents of 2 to 3 at.% in the ZrN $_x$ films were comparable with our previous study using a DCMS system [30,33]. The stoichiometric variable x increased from 0.92 to 1.00, 1.08, and 1.22 with an increasing f from 0.50 to 0.65, 0.75, and 0.85. This was accompanied by a decrease in the deposition rate from 3.8 to 3.4, 3.1, and 1.9 nm/min as only gun 1 was applied with a DC power of 150 W. The decrease in deposition rate with the increasing f level was caused by the reduced ionization and sputtering yield of N $_2$ related to Ar gas [34]. Moreover, the well-known target poisoning effect in reactive sputtering reduced the deposition rate [34–36]. The Zr $_{42}$ N $_{58}$ (1.00) films prepared using an f of 1.00 and sputter power of 150 W on both guns 1 and 2 exhibited an x of 1.38 and a deposition rate of 3.9 nm/min; this deposition rate was almost twice that of the Zr $_{45}$ N $_{55}$ (0.85) films prepared with a high f level and using gun 1 only.

Figure 2a shows the XRD patterns of the ZrN $_x$ films. In a previous study [30], the XRD pattern of the Zr $_{60}$ N $_{40}$ (0.40) films exhibited a ZrN phase [ICDD 00-035-0753] with evident (111), (200), (220), (311), and (222) reflections, which are also shown in Figure 2a for comparison. Ramana et al., [35] reported that ZrN films prepared with an $f < 0.28$ through DCMS were crystalline. The stoichiometric variable x (N/Zr) increased by raising the f level either in DCMS [35] or hollow cathode discharge ion-plating [37]. The Zr $_{52}$ N $_{48}$ (0.50), Zr $_{50}$ N $_{50}$ (0.65), and Zr $_{48}$ N $_{52}$ (0.75) films exhibited a ZrN phase and an extra reflection identified as orthorhombic Zr $_3$ N $_4$ (320) [ICDD 00-051-0646], which was comparable

with findings reported by Signore et al. [17]. The ZrN(200) reflections of the $Zr_{60}N_{40}(0.40)$, $Zr_{52}N_{48}(0.50)$, $Zr_{50}N_{50}(0.65)$, and $Zr_{48}N_{52}(0.75)$ films exhibited lattice constants of 0.4622, 0.4653, 0.4676, and 0.4682 nm, respectively, which implied that at an angle of 2θ , the ZrN(111) reflections should be 33.58° , 33.35° , 33.18° , and 33.14° , respectively; therefore, the overlapped reflections at two-theta angle at around 32° – 33° were fitted as shown in Figure 2b. The ZrN(111) reflections of the $Zr_{45}N_{55}(0.85)$ and $Zr_{42}N_{58}(1.00)$ films, which had no ZrN(200) reflections, were positioned at 33.14° . No Zr_3N_4 reflection was observed for the $Zr_{60}N_{40}(0.40)$ films. The intensity ratio of ZrN(111): $Zr_3N_4(320)$ varied from 54:46 to 49:51, 44:56, 37:63, and 33:67 as the f value increased from 0.50 to 0.65, 0.75, 0.85, and 1.00, which implied that the phase varied from ZrN to Zr_3N_4 -dominant as the f value increased. Figure 2a shows that the insignificant reflection at $2\theta \approx 55^\circ$ for $Zr_{45}N_{55}(0.85)$ and $Zr_{42}N_{58}(1.00)$ films could be a combination of ZrN(220), $Zr_3N_4(251)$, $Zr_3N_4(511)$, and $Zr_3N_4(002)$.

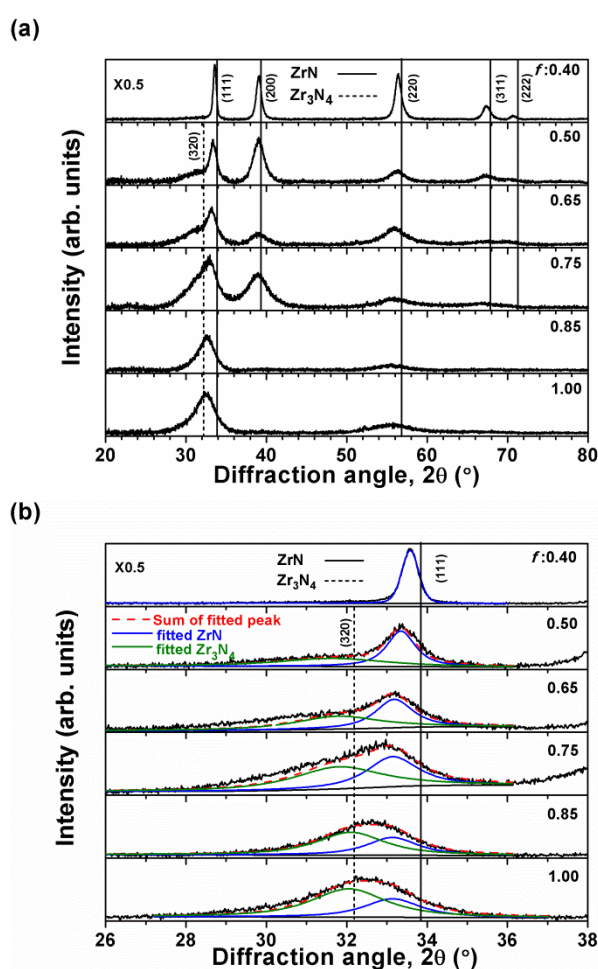


Figure 2. (a) and (b) X-ray diffraction (XRD) patterns of ZrN_x films prepared using various N_2 flow ratios (f).

Figure 3a displays the cross-sectional TEM image of $Zr_{48}N_{52}(0.75)$ films, which exhibit a dense structure. The selected area diffraction pattern (SADP) at the near surface region exhibited ZrN and o- Zr_3N_4 phases. Figure 3b displays a high-resolution TEM image of $Zr_{48}N_{52}(0.75)$ films, which indicates a nanocrystalline structure comprising ZrN and o- Zr_3N_4 crystallites distributed randomly. The fast Fourier transform (FFT) and lattice fringes of selected regions indicated ZrN(200) and o- $Zr_3N_4(320)$ crystallites with d-spacings of 0.225 and 0.276 nm, respectively. Figure 4a illustrates the cross-sectional TEM image of $Zr_{42}N_{58}(1.00)$ films, which SADP is a diffused ring pattern corresponding to o- Zr_3N_4 . Figure 4b displays the high-resolution TEM image of $Zr_{42}N_{58}(1.00)$ films, whereby only o- Zr_3N_4 crystallites are observed.

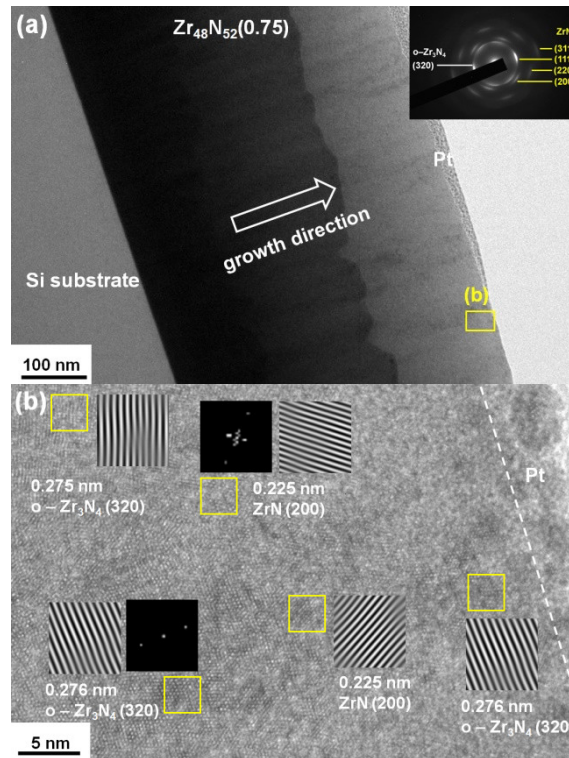


Figure 3. (a) Cross-sectional transmission electron microscope (TEM) image and selected area diffraction pattern (SADP), and (b) a high-resolution image of the $Zr_{48}N_{52}(0.75)$ films.

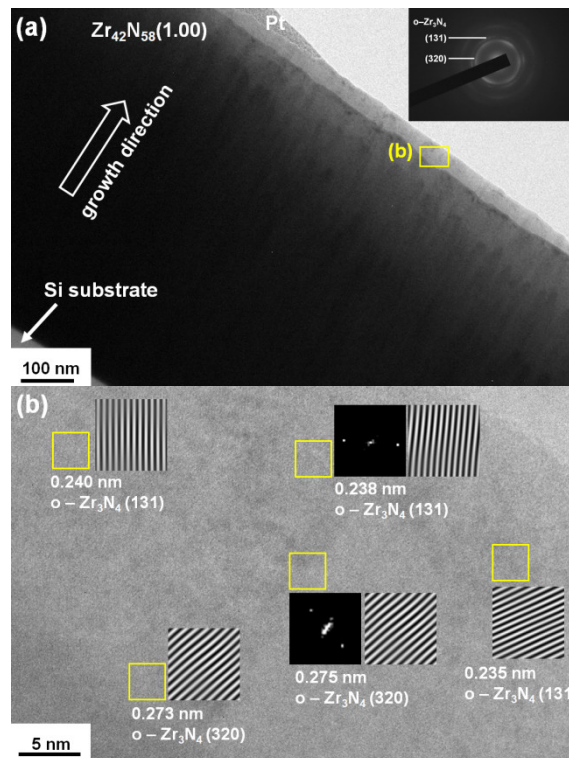


Figure 4. (a) Cross-sectional TEM image and SADP, and (b) high-resolution image of the $Zr_{42}N_{58}(1.00)$ films.

3.2. Bonding Characteristics

The correlation between XRD and XPS analyses was applied to evaluate the mixture constitution of ZrN and Zr_3N_4 [26,38]. Figure 5 exhibits the XPS profiles of the Zr 3d, N 1s, and O 1s core levels of the $Zr_{52}N_{48}(0.50)$ films at sputter depths of 0 to 48 nm. The profiles at the free surface exhibited serious

oxygen pollution because of a high affinity of Zr and O, whereas the profiles beneath the surface were not influenced by O. Figure 6 displays the curve-fitting results of the Zr 3d profiles at a sputter depth of 48 nm for the ZrN_x films. The XPS profiles comprised two doublets, representing Zr–N bonds for ZrN and Zr₃N₄ compounds. The binding energies of the two 3d_{5/2} signals of the Zr₅₂N₄₈(0.50) films were identified as 179.62 ± 0.04 and 181.59 ± 0.03 eV at depths of 8–48 nm for Zr–N in ZrN and Zr₃N₄, respectively. The intensity ratio of ZrN:Zr₃N₄ was 67:33. In our previous study [33], the Zr–N bonds for ZrN and Zr₃N₄ compounds of the Zr₆₀N₄₀(0.40) films were identified as 179.55 and 181.39 eV, respectively. The N profiles of the Zr₅₂N₄₈(0.50) films at depths of 8–48 nm were fitted with two signals with binding energies of 397.16 ± 0.01 and 396.31 ± 0.02 eV, representing N–Zr bonds for ZrN and Zr₃N₄ compounds, respectively. Prieto et al., [24] reported the N 1s values to be 397.3 and 396.4 eV for ZrN and Zr₃N₄, respectively. Furthermore, Prieto et al., [24] concluded that the Zr 3d and N 1s of Zr₃N₄ shifted in opposite directions with respect to those of ZrN, which resulted in an increase of the binding-energy deviation of N 1s, Zr 3d and the Zr₃N₄ becoming an insulator.

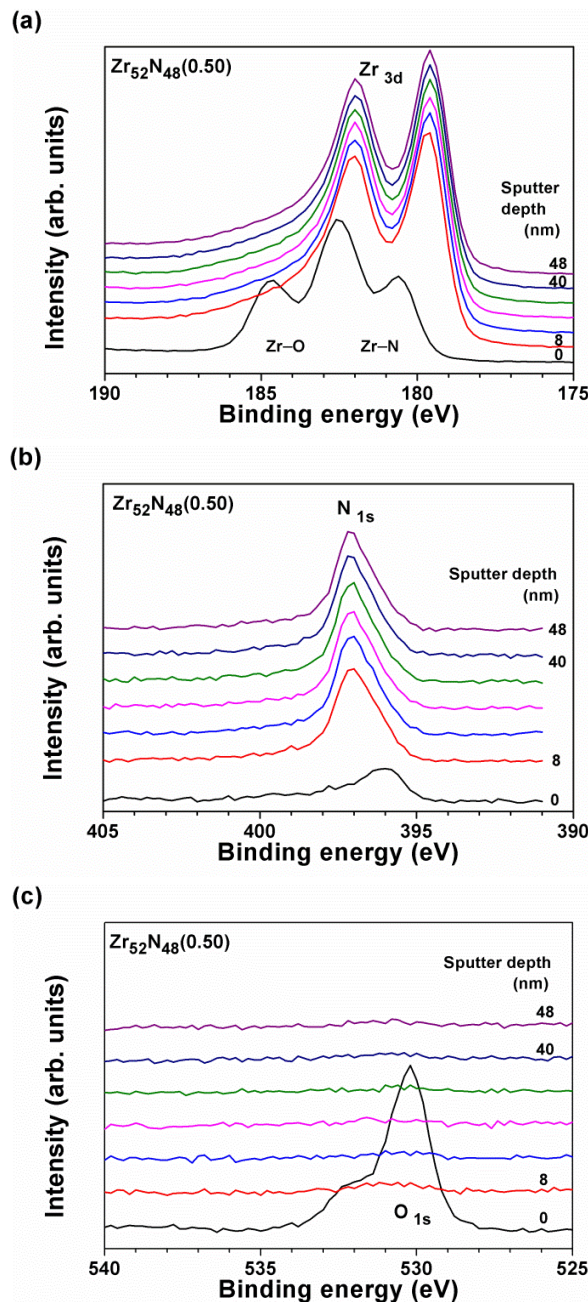


Figure 5. X-ray photoelectron spectroscope (XPS) profiles of the (a) Zr 3d, (b) N 1s, and (c) O 1s core levels of the Zr₅₂N₄₈(0.50) films at depths of 0 to 48 nm (sputter rate = 8 nm/min for SiO₂).

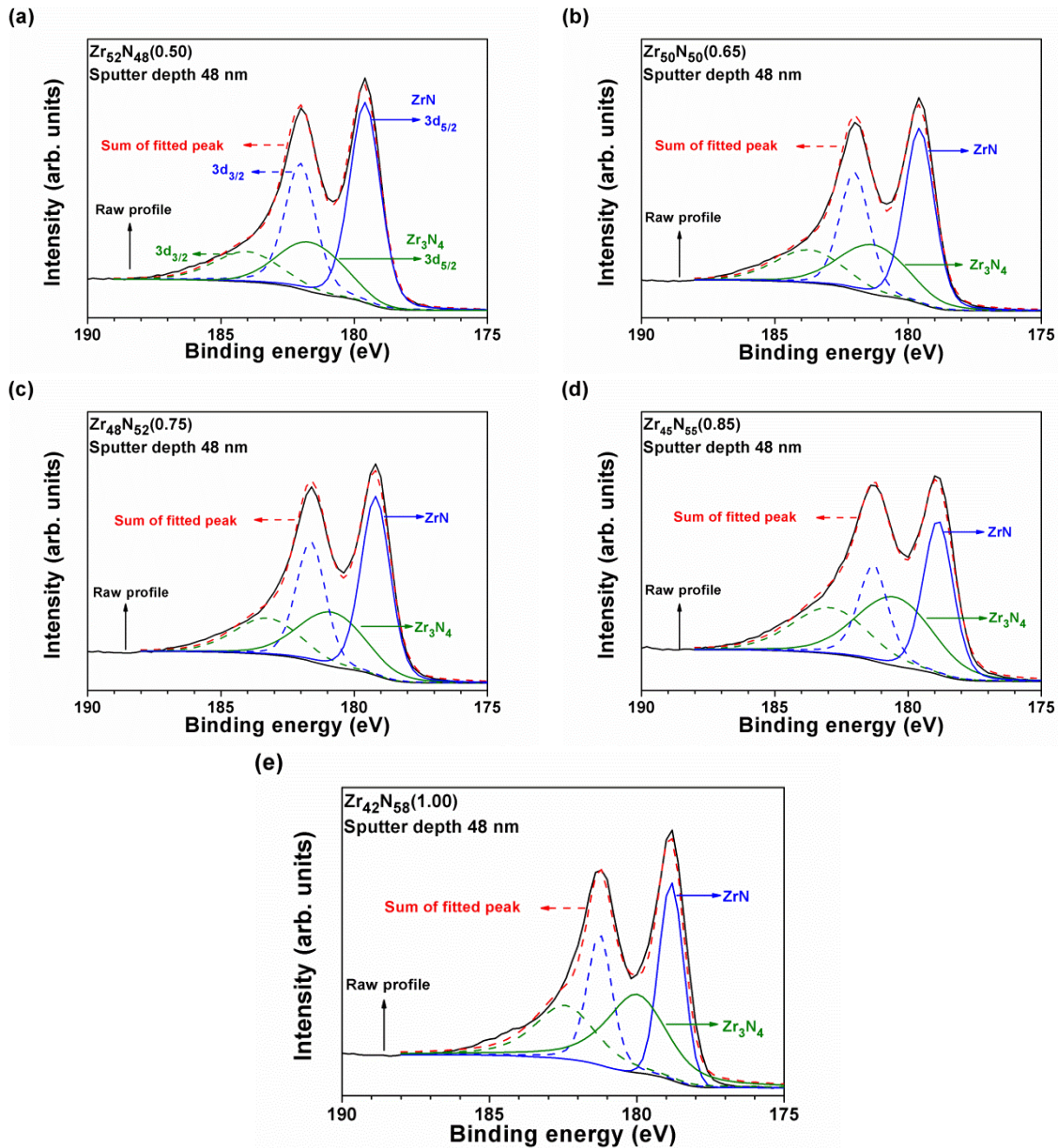


Figure 6. Curve fitting of the Zr $3d$ signals of (a) $Zr_{52}N_{48}(0.50)$, (b) $Zr_{50}N_{50}(0.65)$, (c) $Zr_{48}N_{52}(0.75)$, (d) $Zr_{45}N_{55}(0.85)$, and (e) $Zr_{42}N_{58}(1.00)$ films at depths of 48 nm.

Figure 7 exhibits the XPS profiles of the Zr $3d$ and N $1s$ core levels of the ZrN_x films at a sputter depth of 48 nm. Both the Zr $3d$ and N $1s$ binding energies shifted towards lower levels with increasing N_2 flow ratios. Increasing the N_2 flow ratio to 1.00 decreased the $3d_{5/2}$ signal values of Zr–N bonds to 178.82 ± 0.02 and 180.06 ± 0.04 eV for ZrN and Zr_3N_4 compounds, respectively. Previously reported Zr $3d_{5/2}$ values of Zr–N bonds for ZrN_x were 178.8–179.8 eV [39–42], whereas those of Zr–N bonds for ZrN_{1+x} were 180.3–181.0 eV [40,41]. Table 2 lists the intensity ratios of the two $3d_{5/2}$ signals in the form ZrN: Zr_3N_4 . The ratio of Zr–N bonds in the Zr_3N_4 compound increased with increasing N content in the ZrN_x films, which is an accordance with the observation on phase change by XRD. The ZrN_x films fabricated with an f value higher than 0.85 exhibited Zr_3N_4 -dominant bonding structures.

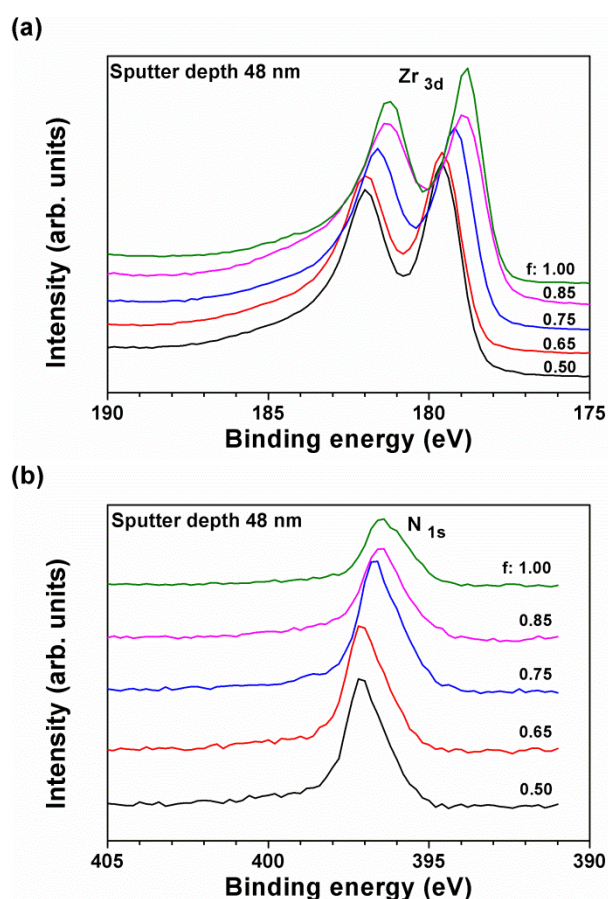


Figure 7. XPS profiles of the (a) Zr 3d and (b) N 1s core levels of the ZrN_x films ($f = 0.50$ – 1.00) at a sputter depth of 48 nm.

Table 2. XPS binding energies and intensity ratios of XRD reflections of the ZrN_x films.

Sample	Zr 3d _{5/2} (eV)	Zr–N(Zr ₃ N ₄)	Intensity Ratio (XPS)	Intensity Ratio (XRD)
	Zr–N(ZrN)		ZrN:Zr ₃ N ₄	ZrN(111):Zr ₃ N ₄ (320)
Zr ₆₀ N ₄₀ (0.40)	179.55 ± 0.06	181.39 ± 0.05	80:20	100:0
Zr ₅₂ N ₄₈ (0.50)	179.62 ± 0.04	181.59 ± 0.03	67:33	54:46
Zr ₅₀ N ₅₀ (0.65)	179.59 ± 0.04	181.29 ± 0.04	59:41	49:51
Zr ₄₈ N ₅₂ (0.75)	179.14 ± 0.03	180.74 ± 0.05	56:44	44:56
Zr ₄₅ N ₅₅ (0.85)	178.84 ± 0.06	180.42 ± 0.04	48:52	37:63
Zr ₄₂ N ₅₈ (1.00)	178.82 ± 0.02	180.06 ± 0.04	44:56	33:67

3.3. Mechanical Properties

Table 3 shows the mechanical properties of ZrN_x films. The ZrN_x films prepared with f levels of 0.50–1.00 exhibited insignificant variations in hardness (18.3–19.0 GPa) and Young's modulus (210–234 GPa), although the residual stress ranged from -0.2 to -1.2 GPa. The Zr₄₅N₅₅(0.85) films exhibited an underestimated hardness of 17.3 GPa, which was attributed to the substrate effect because the indentation depth was 50 nm and the films possessed a low thickness of 348 nm (Table 1), which did not follow the 1/10 rule for accurate examination [43]. Figure 8 displays a representative curve of displacement against load in the nanoindentation test. The Zr₆₀N₄₀(0.40) films with a crystalline ZrN phase and a thickness of 820 nm exhibited a hardness of 21.0 GPa and a Young's modulus of 248 GPa, using an indentation depth of 80 nm accompanied with a residual stress of -0.9 GPa [30]. Qi et al., [5] reported that the hardness values of magnetron-sputtered ZrN films increased from 19.74 to 34.11 GPa as the negative bias voltage changed from 0 to 100 V, resulting in an increase in compressive stress from 0.50 to 4.24 GPa and a decrease in grain size from 43.4 to 11.6 nm. Further increasing the

bias voltage decreased the hardness because of the inverse Hall–Petch effect as the grain size was <10 nm. In the work of Mae et al. [44], the ZrN films fabricated without bias application exhibited a stress ranging from -1 to -2.5 GPa, corresponding to a hardness level of 16–25 GPa depending on the N_2 flow rate in the reactive gas. A higher N_2 flow rate produced films with a lower hardness and stress. In the works of Abadias et al. [45], magnetron-sputtered ZrN films exhibited a hardness of 21.0 GPa. Previous studies indicated that the hardness of o-Zr₃N₄ was similar to that of ZrN [25,46]. In summary, the hardness values of crystalline ZrN films were related to their stressed conditions. The mechanical properties of ZrN_x(*f*) films (*f* = 0.50–1.00) were dominated by the o-Zr₃N₄ phase in a nanocrystalline form accompanied with a low compressive stress level; therefore, the Young’s modulus exhibited a slight decreasing trend and the hardness maintained a constant level as the *f* value increased. Moreover, the evaluation of thin film mechanical properties by nanoindentation technique was affected by the surface roughness [47]. Surface roughness reduced averages and enlarged deviations of nanoindentation hardness and Young’s modulus. All the ZrN_x films exhibited a low average surface roughness of 0.7–1.2 nm (Table 3); therefore, the error in the determination of mechanical properties was negligible.

Table 3. Mechanical properties and surface roughness values of ZrN_x films.

Sample	Hardness (GPa)	Young’s Modulus (GPa)	Stress (GPa)	Roughness (nm)
Zr ₆₀ N ₄₀ (0.40)	21.0 ± 0.3	248 ± 6	−0.9 ± 0.2	1.0 ± 0.0
Zr ₅₂ N ₄₈ (0.50)	18.9 ± 1.0	228 ± 10	−0.6 ± 0.1	1.2 ± 0.0
Zr ₅₀ N ₅₀ (0.65)	19.0 ± 0.5	234 ± 6	−0.2 ± 0.2	1.0 ± 0.1
Zr ₄₈ N ₅₂ (0.75)	18.8 ± 0.9	228 ± 5	−0.5 ± 0.1	0.7 ± 0.0
Zr ₄₅ N ₅₅ (0.85)	17.3 ± 0.4	211 ± 3	−0.7 ± 0.2	0.8 ± 0.1
Zr ₄₂ N ₅₈ (1.00)	18.3 ± 0.9	210 ± 5	−1.2 ± 0.1	1.0 ± 0.0

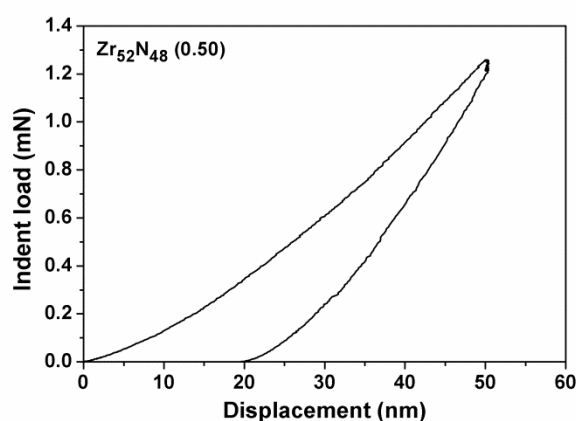


Figure 8. Typical load-displacement curve of nanoindentation tests.

4. Conclusions

ZrN_x(*f*) films with the stoichiometric variable *x* ranging from 0.67 to 1.38 were fabricated on Si substrates through reactive direct current magnetron sputtering by varying the nitrogen flow ratio *f* from 0.4 to 1.0. As nitrogen flow ratio increased, the crystalline structure of the investigated ZrN_x films varied from a cubic ZrN phase for Zr₆₀N₄₀(0.40) films to a mixed nanostructure of cubic ZrN and orthorhombic Zr₃N₄ phases for Zr₅₂N₄₈(0.50), Zr₅₀N₅₀(0.65), and Zr₄₈N₅₂(0.75) films, and to a Zr₃N₄-dominated nanostructure for Zr₄₅N₅₅(0.85) and Zr₄₂N₅₈(1.00) films. The variation in phase from ZrN to Zr₃N₄-dominated, analyzed by X-ray diffraction, was consistent with the alteration in bonding characteristics examined by X-ray photoelectron spectroscopy. The hardness and Young’s modulus of Zr₆₀N₄₀(0.40) films were 21.0 and 248 GPa, respectively. The hardness levels of ZrN_x (*x* = 0.92–1.38) films were 18.3 to 19.0 GPa with a negligible deviation, and the Young’s modulus of the films

decreased slightly from 234 to 210 GPa, which were attributed to the formation of the nanocrystalline α -Zr₃N₄ constitution and the films maintained at a low compressive residual stress level ranged from −0.2 to −1.2 GPa and a low surface roughness of 0.7–1.2 nm.

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Conflicts of Interest: The authors declare no conflicts of interest.

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