Abstract: CrWN coatings were fabricated through a hybrid high-power impulse magnetron sputtering/radio-frequency magnetron sputtering technique. The phase structures, mechanical properties, and tribological characteristics of CrWN coatings prepared with various nitrogen flow ratios ($f_{N_2}$) were investigated. The results indicated that the CrWN coatings prepared at $f_{N_2}$ levels of 0.1 and 0.2 exhibited a Cr$_2$N phase, whereas the coatings prepared at $f_{N_2}$ levels of 0.3 and 0.4 exhibited a CrN phase. These CrWN coatings exhibited hardness values of 16.7–20.2 GPa and Young’s modulus levels of 268–296 GPa, which indicated higher mechanical properties than those of coatings with similar residual stresses prepared through conventional direct current magnetron sputtering. Face-centered cubic (fcc) Cr$_{53}$W$_2$N$_{47}$ coatings with a residual stress of $-0.53$ GPa exhibited the highest wear and scratch resistance. Furthermore, the diffusion barrier performance of fcc CrWN films on Cu metallization was explored, and they exhibited excellent barrier characteristics up to 650 °C.

Keywords: diffusion barrier; HiPIMS; mechanical properties; RFMS

1. Introduction

Transition metal nitride films such as TiN [1], CrN [2,3], TaN [4,5], and W$_2$N [6,7] have been widely utilized as protective coatings in versatile applications, such as hard coatings, diffusion barriers, and corrosion-resistant and wear-resistant layers. Moreover, ternary nitride films such as TiAlN [8], TaZrN [9,10], and CrWN [11] have been developed to enhance the characteristics of the above binary nitride materials. CrWN coatings have been applied as hard coatings [11–15] and protective coatings on die materials for precision molding glass technology [16–19]. In a previous study [15], CrWN coatings manufactured using direct current magnetron sputtering (DCMS) exhibited a wide hardness range of 10.8–27.6 GPa depending on their chemical composition and crystalline structure. The operation of precision molding glass requires molding dies and protective coatings against repeated thermal cycles at 200–600 °C under a low oxygen content atmosphere, implying that CrWN possesses the potential to function as a diffusion barrier for Cu metallization. Cu is the most favorable material for interconnecting ultra-large-scale integrated circuits because of its higher conductivity and superior electromigration resistance compared to Al [20]. Cu diffuses easily into Si and SiO$_2$, which compromises device performance [21,22]. Barrier materials that have been reported to prohibit the diffusion of Cu into Si include transition metals (Cr, Ti, Nb, Ta, and W) [23], bilayers (Ta/Ti) [24], alloys (TiW) [25,26], binary and ternary nitrides (TiN$_x$, TaN$_x$, WN$_x$, RuWN, and WTiN) [26–32], thin film metallic glass (Zr–Cu–Ni–Al–N) [33], and high entropy alloys [34]; and the failure temperatures of these barrier layers exhibited distinct variations in the range of 400–850 °C. Therefore, the successful exploration of new barrier materials is essential in the field of integrated circuits. A qualifying barrier material should exhibit good adhesion to Cu, prevent the diffusion of Cu into Si or the interlayer dielectric (ILD), and be inactive on both Cu and ILD at high
temperatures. CrN has been extensively used for mechanical and corrosion resistance purposes; however, previous reports on its use as a diffusion barrier are scarce [35,36]. CrN can decompose to Cr$_2$N by releasing N$_2$ at temperatures of 500–700 °C because of stress relaxation [37]. W can also be added to CrN to increase oxidation resistance and thermal stability [16,18]. Therefore, the goal of this study was to investigate the mechanical properties and diffusion barrier performance of CrWN coatings.

High-power impulse magnetron sputtering (HiPIMS) exhibits a main feature of a high degree of ionization of sputtered material through the development of a highly dense plasma (~10$^{13}$ ions/cm$^3$) [38–41]. The HiPIMS technique is typified by a low duty cycle of <10%, low repetition frequency of <10 kHz, and high-power densities in the order of kW/cm$^2$ [42]. Therefore, HiPIMS helps to produce coatings with a dense structure and high hardness [43,44]. Moreover, a hybrid HiPIMS/radio-frequency magnetron sputtering (RFMS) process has been previously employed to simultaneously improve the deposition rate and coating quality [45,46]. In this paper, CrWN films were prepared by hybrid HiPIMS/RFMS, the Cu/CrWN/Cr/Si structures were annealed in a vacuum (7 × 10$^{-4}$ Pa) at elevated temperatures for 1 h, and the thermal stability and diffusion barrier characteristics of the CrWN barriers were studied.

2. Materials and Methods

In a hybrid HiPIMS/RFMS apparatus, a target of W (99.95%, 50.8 mm in diameter) was linked to a RF power generator, whereas the target of Cr (99.99%, 76.2 mm in diameter) was attached to a pulse power supply (SPLK 2000A; Shen Chang Electric Co., Ltd., Taipei, Taiwan). The distance between substrates and targets was 12 cm. The substrate holder was rotated at 10 rpm and grounded. In the first part of this study, a Cr interlayer of 100 nm was deposited at 200 W for 10 min under an Ar flow of 30 sccm. Then, CrWN coatings were co-sputtered on Cr interlayers, after flowing N$_2$ and Ar into the vacuum chamber. The total flow rate of N$_2$ and Ar was 30 sccm. The nitrogen flow ratio ($f_{N_2} = N_2/(N_2+Ar)$), ranging from 0.1 to 0.4, was the main process variable. The working pressure was maintained at 0.4 Pa. The power applied to the W ($W_W$) and Cr ($W_{Cr}$) targets was 50 and 500 W, respectively. The deposition times were controlled to form coatings of approximately 1000 nm in thickness. The substrates were silicon and stainless-steel (SUS420) plates. The samples prepared on SUS420 substrates were adopted to evaluate the tribological characteristics, adhesion properties, and wear behavior. Adhesion was tested via a scratch test (Scratch Tester, J & L Tech. Co., Gyeonggi-do, Korea) with a diamond tip 0.2 mm in diameter at a moving speed of 0.01 mm/s. Wear behavior was examined through a pin-on-disc test method with a pin of cemented carbide (WC-6 wt.% Co) and a ball 6 mm in diameter under a normal load of 2 N. The sliding speed was 126 mm/s, the wear track diameter was 4 mm, and the wear length was 200 m. In the second part of this work, two CrWN thin films of 100 nm with a Cr interlayer of 10 nm were fabricated by shortening the deposition times to evaluate their diffusion barrier characteristics, including sheet resistance, phase stability, and elemental diffusion. These samples were covered with a Cu layer (100 nm thick) prepared through DCMS and annealed in a vacuum (7 × 10$^{-4}$ Pa) at 550–650 °C for 1 h.

The elemental compositions were analyzed using a field-emission electron probe microanalyzer (FE-EPMA, JXA-8500F, JEOL, Akishima, Japan). The phases were identified through grazing-incidence X-ray diffraction (GIXRD) using an X-ray diffractometer (X’Pert PRO MPD, PANalytical, Almelo, the Netherlands). Coating thicknesses were examined via cross-sectional images using a field emission scanning electron microscope (FE-SEM, JSM-6701F, JEOL, Akishima, Japan). The nanostructure was observed using transmission electron microscopy (TEM, JEM-2010F, JEOL, Akishima, Japan). The mechanical properties, hardness ($H$), and Young’s modulus ($E$) of the coatings were evaluated using a nanoindentation tester (TI-900 Triboindenter, Hysitron, Minneapolis, MN, USA) and determined using the Oliver and Pharr method [47]. An atomic force microscope (AFM, DI 3100, Bruker, Santa Barbara, CA, USA) recorded the average roughness ($R_a$) and root-mean-
square roughness (Rq). The residual stress of coatings was estimated using the curvature method [48],  

\[ \sigma_{li} = \frac{E_S h_S^2}{6(1 - \nu_S)} R_i, \]  

where \( \sigma_{li} \) is the in-plane stress component in the film, \( l_i \) is the film thickness, \( E_S \) is the Young’s modulus of the Si substrate (130.2 GPa), \( \nu_S \) is the Poisson’s ratio for the Si substrate (0.279), \( h_S \) is the substrate thickness (525 µm), and \( R_i \) is the curvature radius of the film. Wear scars and elemental mapping were observed using SEM (S3400N, Hitachi, Tokyo, Japan) equipped with energy dispersive spectroscopy (EDS, Inca x-sight, Oxford Instruments, Tokyo, Japan). The sheet resistance of the Cu/CrWN/Cr/Si samples was determined using a four-point probe. The sheet resistance can be derived by:  

\[ R = \frac{4.53 V}{I}, \]  

where \( I \) is the applied current, and \( V \) is the measured voltage. The elemental diffusion was examined using an Auger electron spectroscopy (AES, PHI700, ULVAC-PHI, Kanagawa, Japan).

3. Results and Discussion

3.1. CrWN Coatings Co-Sputtered Using Various Nitrogen Flow Rates

Table 1 lists the atomic compositions of the CrWN coatings prepared with an \( f_{N_2} \) of 0.1–0.4. These samples were denoted as Cr\(_{65}\)W\(_4\)N\(_{31}\), Cr\(_{62}\)W\(_3\)N\(_{35}\), Cr\(_{58}\)W\(_2\)N\(_{40}\), and Cr\(_{51}\)W\(_2\)N\(_{47}\) in accordance with their atomic compositions. The N content of the CrWN coatings were increased from 31.0 to 35.0, 39.4, and 46.9 at.% by increasing the nitrogen flow ratio (\( f_{N_2} \)) from 0.1 to 0.2, 0.3, and 0.4, whereas the Cr content exhibited a tendency to decrease from 64.7 to 61.9, 58.1, and 50.6 at.%, and the W content decreased from 4.0 to 2.8, 2.2, and 2.0 at.%. The O contents of these coatings were 0.3 at.%. The deposition rate increased from 12.1 to 14.6 nm/min and then decreased to 11.4 and 10.9 nm/min as \( f_{N_2} \) increased from 0.1 to 0.4 (Table 1).

Table 1. Co-sputtering parameters, atomic compositions, and thicknesses of CrWN coatings.

| Sample | N\(_2\) Flow (sccm) | \( f_{N_2} \) | Atomic Compositions (at.%) | Thickness (nm) | Rate (nm/min) |
|--------|---------------------|---------------|-----------------------------|----------------|--------------|
| Cr\(_{65}\)W\(_4\)N\(_{31}\) | 3 | 0.1 | Cr 64.7 ± 0.6, W 4.0 ± 0.0, N 31.0 ± 0.6, O 0.3 ± 0.1 | 954 | 12.1 |
| Cr\(_{62}\)W\(_3\)N\(_{35}\) | 6 | 0.2 | Cr 61.9 ± 0.5, W 2.8 ± 0.1, N 35.0 ± 0.4, O 0.3 ± 0.2 | 1180 | 14.6 |
| Cr\(_{58}\)W\(_2\)N\(_{40}\) | 9 | 0.3 | Cr 58.1 ± 0.8, W 2.2 ± 0.1, N 39.4 ± 0.7, O 0.3 ± 0.1 | 947 | 11.4 |
| Cr\(_{51}\)W\(_2\)N\(_{47}\) | 12 | 0.4 | Cr 50.6 ± 0.6, W 2.0 ± 0.6, N 46.9 ± 0.5, O 0.3 ± 0.0 | 933 | 10.9 |

\( f_{N_2} \) nitrogen flow ratio.

Figure 1 shows the GIXRD patterns of the CrWN coatings. The coatings prepared with an \( f_{N_2} \) of 0.1 and 0.2 exhibited a hexagonal Cr\(_2\)N phase, whereas the coatings prepared with an \( f_{N_2} \) of 0.3 and 0.4 displayed a face-centered cubic (fcc) CrN phase. As the formation enthalpy of W\(_2\)N (\( \Delta H^0_{298} = -72 \) kJ/mol) is lower than that of CrN (\( -118 \) kJ/mol) and Cr\(_2\)N (\( -126 \) kJ/mol) [6,49], and the W content is low compared to the Cr content, the evolution of the crystalline phase is dominated by the compositions of Cr and N. The phase evolution from Cr\(_2\)N to CrN was accompanied by a decrease in the atomic ratio of Cr/N from 2.09, to 1.77, 1.47, and 1.08 when the \( f_{N_2} \) increased from 0.1, to 0.2, 0.3, and 0.4. Moreover, the reflection Cr\(_2\)N (111) of the Cr\(_{62}\)W\(_3\)N\(_{35}\) coatings shifted toward a lower value compared to that of the Cr\(_{65}\)W\(_4\)N\(_{31}\) coatings, which implies that higher amounts of N atoms were incorporated into the lattice, resulting in an increase in lattice constants. A similar variation was observed in the reflections CrN (111) and (200) of the Cr\(_{51}\)W\(_2\)N\(_{47}\) coatings compared to those of the Cr\(_{58}\)W\(_2\)N\(_{40}\) coatings.
Figure 1. GIXRD patterns of (a) Cr₆₅W₄N₃₁, (b) Cr₆₂W₃N₃₅, (c) Cr₅₈W₂N₄₀, and (d) Cr₅₁W₂N₄₇ coatings.

Figure 2 shows the cross-sectional FE-SEM images of the CrWN coatings. The Cr₆₅W₄N₃₁ coatings revealed an evident columnar structure, whereas the Cr₆₂W₃N₃₅ coatings displayed a much fine columnar structure. By contrast, the Cr₅₈W₂N₄₀, and Cr₅₁W₂N₄₇ coatings revealed an evident columnar structure, whereas the Cr₆₂W₃N₃₅ coatings with a CrN phase exhibited short and disordered grains, similar to those reported by Lin et al. [50]. Figure 3a displays a cross-sectional TEM (XTEM) image of the Cr₅₁W₂N₄₇ coatings, which exhibited a dense and granular structure. The grain size was tens of nanometers. The selected area electron diffraction pattern exhibited CrN (111) and (200) spots. Figure 3b shows lattice fringes of 0.236 and 0.207 nm belonging to CrN (111) and (200) spots. Figure 4 depicts the surface roughness values of the CrWN coatings.

Figure 2. Cross-sectional FE-SEM images of (a) Cr₆₅W₄N₃₁, (b) Cr₆₂W₃N₃₅, (c) Cr₅₈W₂N₄₀, and (d) Cr₅₁W₂N₄₇ coatings.
Figure 2. Cross-sectional FE-SEM images of (a) Cr$_{65}$W$_4$N$_{31}$, (b) Cr$_{62}$W$_3$N$_{35}$, (c) Cr$_{58}$W$_2$N$_{40}$, and (d) Cr$_{51}$W$_2$N$_{47}$ coatings.

Figure 3. (a) XTEM and (b) HRTEM images of the Cr$_{51}$W$_2$N$_{47}$ coatings.

Figure 4. Surface roughness values of the Cr$_{x}$W$_y$N$_z$ coatings.

Figure 5 shows the mechanical properties of the Cr$_{x}$W$_y$N$_z$ coatings. The variation in mechanical properties with N content revealed the combined effects of the phase and residual stress. Figure 6 displays the residual stress of Cr$_{x}$W$_y$N$_z$ coatings, which shows a tendency to vary from tensile (1.30 GPa) to compressive stress (~0.53 GPa) when the N content is increased. Compressive residual stress was beneficial for increasing the hardness [18,51,52]. Figure 7a shows the relationship between the hardness and residual stress of Cr$_{x}$W$_y$N$_z$ coatings. Selected data from a previous study [15] on DCMS-prepared Cr$_{x}$W$_y$N$_z$ coatings dominated by a Cr$_2$N or CrN phase are shown in Figure 7a for comparison. The hardness and residual stress reveal a linear fitting trend. Figure 7b shows the relationship between Young’s modulus and residual stress, and reveals a lower fitting slope compared to those shown in Figure 7a. Therefore, the Cr$_{65}$W$_3$N$_{35}$ coatings showed higher $H$ and $E$ values than those of the Cr$_{63}$W$_4$N$_{31}$ coatings, whereas the Cr$_{51}$W$_2$N$_{47}$ coatings exhibited higher $H$ and $E$ values than those of the Cr$_{58}$W$_2$N$_{40}$ coatings. However, the $H$ values of the Cr$_{62}$W$_3$N$_{35}$ and Cr$_{51}$W$_2$N$_{47}$ coatings were 20.2 and 19.7 GPa, respectively, implying that the H was affected by their phase structures. The Cr$_{62}$W$_3$N$_{35}$ coatings crystallized into a Cr$_2$N phase, whereas the Cr$_{51}$W$_2$N$_{47}$ coatings formed a CrN phase. Previous studies [53–55] have reported that Cr$_2$N is harder than CrN, both in bulk and film form, because of the higher covalent bonding character of Cr$_2$N. Hirota et al. [53] reported hardness values of 14.5 and 11.2 GPa for ceramic Cr$_2$N and CrN, respectively. Hones et al. [54] reported values of 28 and 18 GPa for sputtered Cr$_2$N and CrN films, respectively, whereas 16.1 and 12.5 GPa were obtained in the work of Wei et al. [55]. In a previous study [15], Cr$_{x}$W$_y$N$_z$ coatings with a high W content of 31–57 at.% and fabricated through DCMS revealed an fcc structure and high compressive residual stress in the range from ~2.1 to ~3.0 GPa, accompanied by a high $H$ of 21.1–27.1 GPa and a high $E$ of 241–310 GPa. By contrast, the Cr$_{51}$W$_2$N$_{47}$ coatings prepared through DCMS exhibited a columnar structure accompanied by a low $H$ of 10.8 GPa, a low $E$ of 168 GPa, a high $R_s$ of 6.1 nm, a high $R_q$ of 7.6 nm, and a tensile stress of 0.54 GPa [18]. The DCMS–Cr$_{51}$W$_2$N$_{47}$
coatings exhibited a loose and columnar structure, with a (111) orientation [18], whereas the HiPIMS/RFMS-Cr$_{51}$W$_2$N$_{47}$ coatings revealed a dense and granular structure (Figure 3) with a weak (200) orientation (Figure 1). Hones et al. [11] suggested a small quantity of W stabilized CrWN coatings with a similar weak (200) orientation. Martine et al. [2] reported that CrN films with (200) and (111) orientations demonstrated hardness levels of 18 and 12–14 GPa, respectively. The hybrid HiPIMS/RFMS process in this study enhanced the mechanical properties of the Cr$_{51}$W$_2$N$_{47}$ coatings, even though the W content was low.

![Figure 5](image5.png)

**Figure 5.** $H$ and $E$ levels of CrWN coatings.

![Figure 6](image6.png)

**Figure 6.** Residual stresses of CrWN coatings.

![Figure 7](image7.png)

**Figure 7.** Relationship between (a) hardness and $H^3/E^2$ levels and (b) Young’s modulus against residual stresses of the CrWN coatings.
Figure 8 shows the $H/E$ and $H^3/E^2$ ratios of the CrWN coatings. $H/E$ represents the indicator of elastic strain to failure [56], whereas $H^3/E^2$ denotes the resistance against plastic deformation [57]. The $H^3/E^2$ and residual stress exhibited a linear fitting trend (Figure 7a) similar to those of $H$ and $H/E$ (not shown in this paper) against residual stress. $H/E$ and $H^3/E^2$ were suggested as pointers for fracture toughness, which affected the wear resistance [58]. However, such correlations between $H/E$ and $H^3/E^2$ for toughness were compatible with hard coatings with low plasticity [59]. Figure 9 shows the wear scars of the CrWN coatings. Chippings marks were observed along the wear track of the Cr$_{65}$W$_4$N$_{31}$ coatings. The elemental mapping of Cr and N indicated that the coating was worn out, whereas the Fe signal revealed the exposure of the SUS420 substrate. Similar wear behavior was shown for the Cr$_{62}$W$_3$N$_{35}$ and Cr$_{58}$W$_2$N$_{40}$ coatings with narrow wear widths. The results of wear tests indicated that the Cr$_{65}$W$_4$N$_{31}$, Cr$_{62}$W$_3$N$_{35}$, and Cr$_{58}$W$_2$N$_{40}$ coatings were exhausted with a wear length of 200 m, whereas the Cr$_{51}$W$_2$N$_{47}$ coatings exhibited a low wear rate of $1.4 \times 10^{-6}$ mm$^3$ N$^{-1}$ m$^{-1}$ with a coefficient of friction of 0.60. The DCMS-prepared CrWN coatings with an $H \leq 19.1$ GPa were worn through after wear tests, and the coatings with $H$ values of 20.3–27.0 GPa exhibited wear rates of $3.1–12 \times 10^{-6}$ mm$^3$ N$^{-1}$ m$^{-1}$ [15]. Figure 10 shows the scratch scars of the CrWN coatings. $L_{C1}$ and $L_{C2}$ presented loads inducing cohesive failure and exposing the substrate, respectively [60]. The Cr$_{65}$W$_4$N$_{31}$ coatings exhibited the lowest $L_{C1}$ and $L_{C2}$ values among the tested samples, implying their brittleness. Severe chipping was observed for the Cr$_{65}$W$_4$N$_{31}$ coatings after the normal load reached the $L_{C1}$. Slight chipping was found on the Cr$_{62}$W$_3$N$_{35}$ and Cr$_{58}$W$_2$N$_{40}$ coatings, whereas almost no chipping was detected on the Cr$_{51}$W$_2$N$_{47}$ coatings. The distinct deviations in wear and scratch tests could be attributed to the effect of residual stress. The Cr$_{65}$W$_4$N$_{31}$ coatings exhibited a high tensile residual stress (1.30 GPa), whereas the Cr$_{51}$W$_2$N$_{47}$ coatings demonstrated a compressive residual stress (−0.53 GPa). The $L_{C1}$ was 2 N for the Cr$_{65}$W$_4$N$_{31}$ coatings and 5–7 N for the other three coatings. The $L_{C1}$ and $H/E$ values of these CrWN coatings exhibited similar trends. The $L_{C2}$ increased from 6 N for the Cr$_{65}$W$_4$N$_{31}$ coatings to 15, 22, and 25 N for the Cr$_{62}$W$_3$N$_{35}$, Cr$_{58}$W$_2$N$_{40}$, and Cr$_{51}$W$_2$N$_{47}$ coatings, respectively, implying that the Cr$_{51}$W$_2$N$_{47}$ coatings possessed the highest adhesion strength, agreeing with a high wear resistance. The Cr$_{51}$W$_2$N$_{47}$ coating exhibited the superior mechanical properties and tribological characteristics among the surveyed CrWN coatings.
Table 2. Co-sputtering parameters, atomic compositions, and thicknesses of CrWN films.

Table 2 lists the atomic compositions of the two CrWN films prepared at a thickness of approximately 100 nm and used as diffusion barriers for Cu metallization. In Section 3.1, the coatings prepared using $W_{Cr} = 500$ W, $W_{W} = 50$ W, $f_{N2} = 0.4$, and a deposition time of 85.6 min exhibited a composition of Cr$_{51}$W$_2$N$_{47}$, whereas the composition became Cr$_{59}$W$_2$N$_{39}$ as the deposition time was reduced to 6.7 min. This result can be attributed to the overestimation of Cr content because of a low thickness of 108 nm for the CrWN films accompanied by a Cr interlayer of 10 nm. In addition, the Cr$_{54}$W$_6$N$_{40}$ samples were prepared using a higher W$_W$ of 100 W. Figure 11 shows the sheet resistance of the Cu/CrWN/Cr/Si samples. The 550 °C annealed samples exhibited lower sheet resistances than those at the as-deposited state, which was attributed to the defect annihilation and grain growth of Cu films [29,61]. The sheet resistance increased slightly when the samples were annealed at 600 and 650 °C, whereas an abrupt increase was observed when the annealing temperature was set to 700 °C, which implied the formation of Cu$_3$Si [61]. Figures 12 and 13 show the GIXRD patterns of the Cu/Cr$_{65}$W$_4$N$_{31}$/Cr/Si and Cu/Cr$_{51}$W$_2$N$_{47}$/Cr/Si samples annealed at 550–650 °C, respectively, and no reflection from Cu-silicide is observed. The as-deposited samples exhibited CrN and Cu phases, whereas a Cr$_2$N phase was observed after annealing at 550–650 °C. The diffusion barrier performance of the Cu/CrWN/Cr/Si samples was further examined through the AES depth profiles of the annealed samples.

Figure 9. Wear scars and elemental mapping of (a) Cr$_{65}$W$_4$N$_{31}$, (b) Cr$_{62}$W$_3$N$_{35}$, (c) Cr$_{58}$W$_2$N$_{40}$, and (d) Cr$_{51}$W$_2$N$_{47}$ coatings.

Figure 10. Scratch scars of the CrWN coatings.

3.2. Diffusion Barriers

The coatings prepared using $W_{Cr} = 500$ W, $W_{W} = 50$ W, $f_{N2} = 0.4$, and a deposition time of 85.6 min exhibited a composition of Cr$_{51}$W$_2$N$_{47}$, whereas the composition became Cr$_{59}$W$_2$N$_{39}$ as the deposition time was reduced to 6.7 min. This result can be attributed to the overestimation of Cr content because of a low thickness of 108 nm for the CrWN films accompanied by a Cr interlayer of 10 nm. In addition, the Cr$_{54}$W$_6$N$_{40}$ samples were prepared using a higher $W_{W}$ of 100 W. Figure 11 shows the sheet resistance of the Cu/CrWN/Cr/Si samples. The 550 °C annealed samples exhibited lower sheet resistances than those at the as-deposited state, which was attributed to the defect annihilation and grain growth of Cu films [29,61]. The sheet resistance increased slightly when the samples were annealed at 600 and 650 °C, whereas an abrupt increase was observed when the annealing temperature was set to 700 °C, which implied the formation of Cu$_3$Si [61]. Figures 12 and 13 show the GIXRD patterns of the Cu/Cr$_{65}$W$_4$N$_{31}$/Cr/Si and Cu/Cr$_{51}$W$_2$N$_{47}$/Cr/Si samples annealed at 550–650 °C, respectively, and no reflection from Cu-silicide is observed. The as-deposited samples exhibited CrN and Cu phases, whereas a Cr$_2$N phase was observed after annealing at 550–650 °C. The diffusion barrier performance of the Cu/CrWN/Cr/Si samples was further examined through the AES depth profiles of the annealed samples.
Table 2. Co-sputtering parameters, atomic compositions, and thicknesses of CrWN films.

| Sample       | \( W_{Cr} \) (W) | \( W_W \) (W) | \( f_{N2} \) | Cr (W) | W (W) | N (W) | O (W) | Thickness (nm) |
|--------------|-------------------|----------------|-------------|--------|--------|-------|-------|----------------|
| Cr\(_{59}\)W\(_{2}\)N\(_{39}\) | 500               | 50             | 0.4         | 57.5 ± 0.5 | 2.3 ± 0.0 | 37.8 ± 0.5 | 2.4 ± 0.0 | 108            |
| Cr\(_{54}\)W\(_{6}\)N\(_{40}\) | 500               | 100            | 0.4         | 52.8 ± 0.5 | 6.5 ± 0.2 | 39.1 ± 0.8 | 1.6 ± 0.2 | 103            |

\(^1 \) \( W_{Cr} \): power on Cr target; \(^2 \) \( W_W \): power on W target.

Figure 11. Sheet resistance of the annealed Cu/CrWN/Cr/Si samples.

Figure 12. GIXRD patterns of (a) as-deposited and (b–d) annealed Cu/Cr\(_{59}\)W\(_{2}\)N\(_{39}\)/Cr/Si samples.

Figure 13. GIXRD patterns of (a) as-deposited and (b–d) annealed Cu/Cr\(_{54}\)W\(_{6}\)N\(_{40}\)/Cr/Si samples.
Figures 14 and 15 show the AES depth profiles of the as-deposited and annealed Cu/Cr$_{59}$W$_2$N$_{39}$/Cr/Si and Cu/Cr$_{54}$W$_6$N$_{40}$/Cr/Si samples, respectively. The main variation between the as-deposited and annealed samples occurred at the interlayer. The original Cr interlayer evolved into an interdiffusion zone consisting of Cr, N, and Si. The interdiffusion between Si/Cr interface was reported at 450 °C [62]. Cu diffused into a shallow depth of the CrWN films at 650 °C. The CrWN films played the role of a diffusion barrier up to 650 °C after annealing for 1 h.

![AES depth profiles of (a) as-deposited, (b) 600 °C, and (c) 650 °C annealed Cu/Cr$_{59}$W$_2$N$_{39}$/Cr/Si samples.](image1)

![AES depth profiles of (a) as-deposited, (b) 600 °C, and (c) 650 °C annealed Cu/Cr$_{54}$W$_6$N$_{40}$/Cr/Si samples.](image2)

**Figure 14.** AES depth profiles of (a) as-deposited, (b) 600 °C, and (c) 650 °C annealed Cu/Cr$_{59}$W$_2$N$_{39}$/Cr/Si samples. (Annealed in vacuum for 1 h).

**Figure 15.** Cont.
Figure 14. AES depth profiles of (a) as-deposited, (b) 600 °C, and (c) 650 °C annealed Cu/Cr 59W2N39/Cr/Si samples. (Annealed in vacuum for 1 h).

Figure 15. AES depth profiles of (a) as-deposited, (b) 600 °C, and (c) 650 °C annealed Cu/Cr 54W6N40/Cr/Si samples. (Annealed in vacuum for 1 h).

4. Conclusions

CrWN coatings were successively fabricated through a hybrid HiPIMS/RFMS process. The N content of the CrWN coatings increased when the \( f_{N_2} \) was increased, accompanied by structural variation from the Cr\(_2\)N to CrN phase. The principal conclusions of this study can be summarized as:

1. The hybrid HiPIMS/RFMS process formed CrWN coatings with a dense structure and a smooth surface.
2. The mechanical properties, hardness and Young’s modulus, of the CrWN coatings were affected by the crystalline phase and residual stress. The \( \text{Cr}_{51}\text{W}_{2}\text{N}_{47} \) coatings exhibited a granular structure, revealing enhanced mechanical properties (\( H: 19.7 \text{ GPa}, \ E: 296 \text{ GPa} \)) and reduced surface roughness values (\( R_a: 2.6 \text{ nm}, \ R_q: 3.3 \text{ nm} \)), accompanied by a compressive residual stress of \(-0.53 \text{ GPa} \).
3. The tribological characteristics, wear resistance, and scratch behavior of the CrWN coatings were affected by residual stress. The \( \text{Cr}_{51}\text{W}_{2}\text{N}_{47} \) coatings with a compressive residual stress exhibited superior tribological characteristics compared to those CrWN coatings revealing tensile residual stresses.
4. The application of CrWN films as a diffusion barrier on Cu metallization was practiced by annealing up to 650 °C in a vacuum for 1 h.

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