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# Effect of bias voltage on the growth of super-hard (AlCrTiVZr)N high-entropy alloy nitride films synthesized by high power impulse magnetron sputtering

# Yi Xu, Guodong Li, Guang Li, Fangyuan Gao, Yuan Xia

Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, PR China

Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

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# ABSTRACT

The purpose of this paper is to explore the effect of bias voltage on plasma discharge characteristics, element concentration, microstructure, morphology, and mechanical properties of super-hard (AlCrTiVZr)N high-entropy alloy nitride (HEAN) films synthesized by high power impulse magnetron sputtering (HiPIMS). Results show that all HiPIMS-deposited (AlCrTiVZr)N films and the DCMS reference sample present a single NaCl-type FCC structure. Compared with DCMS, HiPIMS can produce a higher ionization fraction of the HEA target elements, thereby improving the structure and mechanical properties, while reducing the deposition rate. With increasing bias voltage in HiPIMS, the ion bombardment is continuously enhanced due to the increasing flux and energy of ionized particles reaching the films. The altered plasma environment splits the growth of (AlCrTiVZr)N films into two regions: The bias voltages of 0 V to -150 V offer a moderate ion bombardment effect, while further increasing bias voltage up to -200 V makes the ion bombardment effect excessive. It is observed that the (AlCrTiVZr)N films deposited at -150 V have a compact and featureless structure with preferred orientation of (111), the smallest grain size of 11.3 nm, a high residual compressive stress of -1.67GPa, thereby exhibiting the highest hardness of 48.3 GPa which attains the super-hard grade.

# 1. Introduction

High-entropy alloy nitride (HEAN) films, as a new research hotspot, have their roots in the bulk HEAs which acquired tremendous research interests over the last decade [1,2]. From the aspect of thermodynamics, owing to the high-mixing entropy effect resulted from the increased number of principal component elements, HEAN films are more inclined to form multi-element solid-solution phase instead of complex intermetallic compounds [3]. From the aspect of kinetics, the severe lattice distortion caused by the large difference in atomic size lowers cooperative diffusion of different elements, thus promoting the formation of nanocrystalline and even amorphous structures [4]. The resulting HEAN films exhibit many extraordinary features, such as superior hardness [5], excellent wear and corrosion resistance [6,7], strong diffusion barrier capabilities [8], etc., which traditional nitride films are incomparable with. Therefore, HEAN films show promising potential to serve as the hard films in the cutting tools and diffusion barrier layers in the field of Cu interconnects [9,10]. Generally, a variety of HEAN films are

\* Corresponding author. *E-mail address:* xia@imech.ac.cn (Y. Xia).

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synthesized by magnetron sputtering (MS), a well-established physical vapor deposition (PVD) method, including direct current and radio-frequency MS [11,12]. However, the deposition of HEAN films using MS faces a major challenge of the relatively low-level ionization degree of sputtered particles (usually not exceed 5%)[13,14], which often induces the generation of a lot of defects, such as pinholes and large gaps, thereby weakening the mechanical properties of the films. Therefore, to obtain HEAN films with desirable mechanical performance, a synthetization technique capable of offering high-density plasma environment and subsequently controlling the film growth process is urgently required.

As an advanced PVD technology, high power impulse magnetron sputtering (HiPIMS) technique has been proved to be advantageous in synthesizing films as smooth as MS-deposited films, and as dense as filtered cathodic vacuum arc (FCVA)-deposited films [15–17]. By applying short unipolar pulses with high peak power density (1–3 kW/ cm<sup>2</sup>), low frequency (<10 kHz) and duty cycle (<10%) to the target, an ultra-dense plasma with electron density up to  $10^{19}m^{-3}$  can be





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produced, which is several orders of magnitude higher than that in MS [18]. It is well known that in a high-density plasma environment, intensive ion bombardment effect as well as enhanced adatom mobility are expected to take place, which can enable the synthesization of nearly void-free and ultra-smooth films, making it possible to tailor the phase composition, microstructure, morphology as well as mechanical properties [19]. In order to obtain these desirable benefits, the ion bombardment on the films over the HiPIMS deposition process should be effectively controlled. For this purpose, the simplest method is to utilize the substrate bias voltage to force ionized particles to move toward the films as well as to control the kinetic energy of the ionized particles. As Zhou et al. [20] observed, Al<sub>2</sub>O<sub>3</sub> films synthesized by HiPIMS at different bias voltages demonstrated that the increase of bias voltage could promote the weakly crystalline films to evolve to fully crystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> films. According to Hajihoseini et al. [21], increasing the bias voltage from 0 V to -200 V contributed to an apparent decrease in the surface roughness of HiPIMS-deposited VN films and a shift in the preferred orientation from (111) to (200). Ma et al. [22] investigated the TiAlSiN films synthesized by HiPIMS with varying bias voltages. By applying an increasing bias voltage, they observed an increase in the target current from 118A to 165 A, a transformation in cross-sectional microstructure from continuous column to the fully compact glassy feature, and an increase in hardness from 30 GPa to 42 GPa. Unfortunately, so far, the effect of bias voltage on microstructure, mechanical properties, and corresponding plasma discharge characteristics of HiPIMS-deposited HEAN films have yet to be explored.

In our previous work [23], a novel super-hard HEAN films, (AlCr-TiVZr)N films have been synthesized by HiPIMS. To better understand the growth mechanism of (AlCrTiVZr)N films in the HiPIMS process, different bias voltages were employed to control the ion bombardment on the films in this work. The bias voltage ranging from 0 V to -200 V was applied to investigate its effect on plasma discharge characteristics, element composition, microstructure, morphology, and mechanical properties of these films. Meanwhile, (AlCrTiVZr)N films deposited by DCMS were provided as a reference sample to probe into the differences between HiPIMS and DCMS techniques.

#### 2. Experimental procedure

# 2.1. Films preparation

The synthesization of (AlCrTiVZr)N films were performed in a homemade PVD apparatus equipped with HiPIMS (HighPulse 4002, Huttinger Electronic) and DCMS (MSP-20D, Pulse Tech) power supplies. The polished WC-CO cutting tool inserts (YT-15, ZCC) were chosen as the samples. And the thin single-crystalline Si wafers (100) of  $300 \pm 10 \,\mu\text{m}$ in thickness were also selected as samples to determine the residual stress. Before being placed in the vacuum chamber, all samples were cleaned with acetone and later ethanol in an ultrasonic bath, followed by rinsing in de-ionized water. A HEA mosaic target (3 in.), consisting of fan-shaped AlCr, TiZr and V targets at different angles (all 99.99% purity), was specifically designed for the equimolar sputtering of Al, Cr, Ti, V and Zr elements. Detailed information of this HEA mosaic target can be found in previous publications [23].

Prior to the deposition, the vacuum chamber was pumped down to 3  $\times 10^{-3}$  Pa. The samples were further sputter-cleaned by Ar<sup>+</sup> ion bombardment at -700 V for 15 min to remove surface impurities. To stabilize the deposition conditions, the pre-sputtering for the target should be carried out for 3 min before each deposition process in order to remove the contaminants formed on the target surface. During the film growth, the total deposition pressure was 0.55 Pa and the gas mixture consisted of Ar and N<sub>2</sub> (both 99.999% purity), where the gas flow rate of Ar and N<sub>2</sub> was 155 sccm and 15 sccm, respectively. The bias voltages of 0 V (grounded, referred to as Sample H-0), -50 V (H-50), -100 V (H-100), -150 V (H-150), -200 V (H-200) were applied to the substrate. Meanwhile, the DCMS-deposited (AlCrTiVZr)N films (D-100)

were used as a reference sample, which were prepared using a bias voltage of -100 V and the same time-averaged power as the sample H-100 did. No sample rotation and external heating system were employed. The detailed deposition conditions, including the pulsing parameters of HiPIMS, were summarized in Table 1.

#### 2.2. Plasma discharge characteristics

The HiPIMS target current and substrate current time characteristics were detected by a current probe sensor (CWT1B, PEM), while the voltage-time characteristics of the HiPIMS target were measured by a high voltage probe (IHVP250, Tektronix). These in-situ waveforms during deposition processes were monitored with a digital oscilloscope (TDS1002B, Tektronix). To perform the qualitative analysis of excited neutral and ionized particles in the HiPIMS and DCMS discharge, timeaveraged optical emission spectroscopy (OES) investigations were conducted based on a plasma emission monitor (FT-H5, Nava Fabrica Flotron<sup>™</sup>). The signal collector was placed on the right side of the HEA target with a distance of 120 mm in the radial direction and a distance of 10 mm in the normal direction. The optical emission spectrums were recorded in the wavelength range of 240 nm to 540 nm as the optical emission lines of the HEA target elements were mainly distributed in this region, and the OES integration time was set to be 30 ms. The representative optical emission lines of Al, Cr, Ti, V and Zr with excited neutral and ionized states were summarized in Table 2.

#### 2.3. Films characterization

The compositional analysis of the (AlCrTiVZr)N films was conducted using field-emission electron probe microanalysis (EPMA, JAX8230, JEOL). The deposition rate and cross-sectional morphology were investigated by field emission scanning electron microscope (FE-SEM, SUPRA55, ZEISS). In order to avoid interference information from the substrate, the crystal structure of the films was confirmed by means of a grazing-incidence (1°) X-ray diffraction (GIXRD, D/MAX 2500, RIGAKU) with Cu K $\alpha$  source, whose scanning speeding was 2°/min. Further, from the full width at half-maximum, the average grain size of films was calculated by Debye-Scherrer's formula [5,24]. Surface roughness and morphology (5  $\times$  5  $\mu$ m<sup>2</sup> scan size) were observed by atomic force microscope (AFM, MODE 8, VECO). The hardness and elastic modulus were evaluated based on the load-displacement curves measured by a nano-indentation tester (G200, AGILENT) in the continuous stiffness mode. For all deposited films, the penetration depth of the indenter was set to be 300 nm (below 10% of films thickness) for

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Details	of c	leposition	conditions.
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Parameter	Value	
	HiPIMS (Sample H-0/50/100/ 150/200)	DCMS (Sample D- 100)
Target-Substrate Distance	75	75
(mm)		
Ar / N2 flow rate (sccm)	155/15	155/15
Deposition Pressure (Pa)	0.55	0.55
Deposition Time (min)	60	60
Bias Voltage (-V)	0/50/100/150/200	100
HiPIMS Pulse Frequency (Hz)	200	/
HiPIMS Pulse Duration (µs)	100	/
HiPIMS Pulse Target	560	/
Voltage (-V)		
HiPIMS Peak Target	86/93/98/103/110	/
Current (A)		
DCMS Voltage (-V)	/	436
DCMS Current (A)	/	1.8
Time Averaged Power	0.69/0.73/0.78/0.81/0.86	0.78
(kW)		

#### Table 2

Summary of the representative optical emission lines of the HEA target elements in the wavelength range of 240 nm to 540 nm.

Particle	Wavelength (nm)	Wavelength (nm)		
	Excited neutral state	Ionized state		
Al [53,54]	310/396.1	390.2/465.4		
Cr [55,56]	425.6/507.4	267.7/284.1		
Ti [57,58]	520.8/365.4	323.2/336.8		
V [54–59]	375.2/440	320.8/311.9		
Zr [60,61]	386.4/515.5	292.7/349.6		

the purpose of avoiding the substrate effect. The residual stress  $\sigma$  was determined by utilizing the optical profilometer (GT-K, BRUKER) to measure the curvature of films-substrate and applying Stoney's formula for calculation.

#### 3. Results and discussion

#### 3.1. Plasma emission characteristics comparison: HiPIMS vs. DCMS

To compare the difference between the ionization states of the HEA target elements in the HiPIMS and that in the DCMS, OES investigations of the plasma discharge have been carried out during the deposition of Sample D-100 and H-100, which are operated under the same deposition conditions (see Fig. 1). It can be seen that there is almost no difference in terms of existing species. In both DCMS and HiPIMS, the clearly observed optical emission lines come from not only excited neutral particles but also ionized ones. However, according to the OES spectrum in Fig. 1(a), the DCMS discharge mainly reveals the presence of excited neutral particles as well as a small amount of ionized particles, including  $Al^+(390.2 \text{ nm}/465.4 \text{ nm}), \text{ Ti}^+$  (336.8 nm),  $V^+$  (320.8 nm) and  $Zr^+$ (349.6 nm). Notably, the optical emission lines of ionized Cr<sup>+</sup> particles are not detected, which implies that the Cr element exists mainly in its neutral state during this process. This is apparently attributed to the fact that the first ionization potential of Cr element is higher than that of Al, Zr and V, and the collisional ionization cross-section of Cr is lower than that of Ti [25]. In contrast, as shown in Fig. 1(b), there is a sharp Cr<sup>+</sup> optical emission line (267.7 nm/284.1 nm) in the OES spectrum acquired during HIPIMS process, where is accompanied with other optical emission lines attributed to ionized Ti<sup>+</sup> (323.2 nm), V<sup>+</sup> (311.9 nm) and  $Zr^+$  (292.7 nm) particles. Moreover, the intensities of the optical emission lines from the ionized Al<sup>+</sup>, Ti<sup>+</sup>, V<sup>+</sup> and Zr<sup>+</sup> particles (also existing in the DCMS) all significantly increase. The results of OES investigations are consistent with a higher peak current density of 2.15A/cm<sup>2</sup> in

HiPIMS (H-100) compared to that of  $0.04 \text{ A/cm}^2$  in DCMS (D-100), and confirm a higher ionization fraction of the HEA target elements in HiPIMS.

#### 3.2. Plasma discharge characteristics of HiPIMS

Fig. 2 presents the temporal evolutions of the target current waveforms under different bias voltages, while the target voltage waveform at a bias voltage of -100 V is provided for reference. Interestingly, it can be observed that the peak target current increases sharply from 86 A to 110 A with increasing bias voltage from 0 V to -200 V. In fact, the target current consists of the collected ion current *I*<sub>ion</sub>, plasma electron current  $I_e$ , secondary emission electron current  $I_{sec}$  and the displacement current  $I_{disp}$  [26]. As the target voltages during all deposition processes are -560 V, the HEA target has a constant secondary electron yield, which keeps the secondary emission electron current Isec unchanged. By applying pulse voltage to the target without plasma, the displacement current Idisp waveforms can be measured, whose results demonstrate that the target current waveforms remain the same after the displacement current waveforms are removed. Therefore, the increase in the target current with increasing bias voltage is resulted from the collected ion current  $I_{ion}$  and plasma electron current  $I_e$ , that is, the plasma density. With the increase of bias voltage, more electrons are apt to move



**Fig. 2.** The temporal evolution of target current waveforms under different bias voltages and the target voltage waveform at a bias voltage of -100 V during a pulsed period.



Fig. 1. Optical emission spectrums obtained during (AlCrTiVZr)N films deposition using DCMS (a) and HiPIMS (b), both of which were conducted at a time-averaged power of 0.78 W, a bias voltage of -100 V and a deposition pressure of 0.55 Pa.

towards the target and get more energy under the effect of an enhanced electric field in the plasma sheath around the substrate, which leads to an increase in density and energy for electrons in the target region. Thus, more high-energy electrons will be trapped by the magnetron, which dramatically increases the probability of ionization collisions between electrons and neutral particles, thereby resulting in an increase of the plasma density as well as its target current accompanied.

The current waveforms collected on the substrate under different bias voltages are given in Fig. 3. It can be observed that the substrate current contains not only ionic current but also electronic current. Meanwhile, under different bias voltages, all substrate current waveforms exhibit pulse characteristics, and gradually reach their peak values before the end of pulse. The substrate current waveform can be explained from the aspect of particle movement. At the initial stage of pulse, the electronic current is captured firstly since electrons have a much higher thermal velocity due to their relatively low mass. As time elapses, under the influence of bias voltage, the ion loss to the substrate increases while electrons in the plasma sheath are repelled. Subsequently, a peak in the ionic current appears and the plasma becomes ion rich. The plasma sheath thickness is correlated to Debye length, which is proportion to the  $\sqrt{T_e}$  ( $T_e$ : electron temperature) and inversely proportion to the  $\sqrt{n_0}(n_0)$ : plasma density) [27]. According to the previous reports by Seo et.al [28] and Liu et.al [29,30], the increase of bias voltage has a small influence on the electron temperature  $T_e$ . In addition, as mentioned above, the plasma density  $n_0$  increases with increasing bias voltage. As a result, the electric field in the plasma sheath around the substrate is enhanced with the increase of bias voltage due to the decrease of Debye length and the increase of bias voltage. In such situation, more electrons are repelled and more ions can reach the substrate. Meanwhile, the velocity of ions reaching the substrate increases. Accordingly, the increasing bias voltage from 0 V to -200 V leads to an increase in peak ionic current from 0.033A to 3.17A. From the perspective of film growth, the increase of bias voltage and substrate current indicates an increase in flux and energy of ionized particles reaching the films, which can greatly enhance the ion bombardment effect.

Furthermore, it should be noted that there are two remarkable differences in the current waveforms. Firstly, when bias voltage is -50 V, an ionic current is monitored again even after pulse-off. The occurrence of a late peak can be attributed to a relatively low bias voltage of -50 V, which fails to provide enough energy for low-energy ionized particles in the plasma to reach the substrate during a pulsed period [31]. Secondly, with the bias voltage increasing from -150 V to -200 V, the substrate



current is close to the saturation and just shows a small increase. On the one hand, almost no electrons can reach the substrate at higher bias voltage. On the other hand, the increment of the velocity of ions reaching the substrate is proportion to the  $\sqrt{V}(V)$  bias voltage). This means the velocity of the ions reaching the substrate increases slightly at higher bias voltage. So at higher bias voltage, the velocity of the ions reaching the substrate is mainly determined by the velocity of ions entering into the plasma sheath, that is, the Bohm velocity which is proportion to the  $\sqrt{T_e}$  [32]. As mentioned above, the increase of bias voltage has a small influence on the electron temperature  $T_{e}$ . Therefore, the plasma density  $n_0$  becomes the dominant factor for the increase of substrate current. Considering the small size of the samples, the substrate current just increases slightly at the bias voltage higher than -150 V. It is worth stressing that although the substrate current achieves a state of saturation, the kinetic energy of ionized particles still continues to increase, which also can positively affect the ion bombardment effect.

#### 3.3. Element concentration and deposition rate

The atomic concentrations of all elements in HiPIMS-deposited (AlCrTiVZr)N films under different bias voltages are displayed in Fig. 4. It can be found that the ratio of atomic concentrations of Al, Cr, Ti, V and Zr in the films deviates slightly from that in the HEA target. It is probably caused by the difference in the sputtering yield of each fanshaped target, thereby leading to the nonuniformity of the magnetic field on the target surface with the increase of sputtering time [23]. Overall, increasing bias voltage from 0 V to -200 V causes a remarkable decrease in N atomic concentration, but a slight increase of atomic concentrations of HEA target elements. A possible explanation of this phenomenon is that N, the lightest element in the films, is much easier to be re-sputtered from the films at higher bias voltage. Meanwhile, the entrapped extra N atoms may exist in non-equilibrium sites because of the non-equilibrium deposition process for HiPIMS [33]. The enhanced ion bombardment effect caused by the increasing bias voltage can provide N atoms more energy so that they escape from the surface. Additionally, of all HEA target elements, only the atomic concentration of Al is found to decrease slightly at the bias voltages higher than -100 V, which can be attributed to the fact that Al has the lowest weight and relatively high sputtering yield in HEA target elements. At higher bias voltage, the former makes Al atoms easier to be scattered by high-energy ionized particles during the flight from target to the substrate, while the



Fig. 4. Atomic concentration of HiPIMS-deposited (AlCrTiVZr)N films determined by EPMA under different bias voltages and the DCMS reference sample.

latter promotes the preferential re-sputtering of Al atoms from the films by high-energy ionized particles.

Our previous studies [23] have shown that the microstructure and mechanical properties are strongly dependent on N atomic concentration in the (AlCrTiVZr)N films. Although increasing bias voltage from 0 V to -200 V causes a remarkable decrease in N atomic concentration (52 at.% to 43 at.%) in this paper, all (AlCrTiVZr)N films still exhibit a single NaCl-type FCC structure and no amorphization phenomenon is discovered (Fig. 6). The hardness of films shows a significant increasing trend with the increase of bias voltage (Fig. 10). These results are very different from the conclusion in our previous paper. Considering that the increase of bias voltage results in an increase in flux and energy of ionized particles reaching the films, the ion bombardment effect is regarded as the main factor affecting the microstructure and properties of (AlCrTiVZr)N films in the following discussion.

Fig. 5 illustrates the deposition rate of HiPIMS-deposited (AlCrTiVZr) N films under different bias voltages and the DCMS reference sample. Although HiPIMS (H-100, 63.3 nm/min) and DCMS (D-100,78.5 nm/ min) are operated under the same deposition conditions, a significant decrease in deposition rate is explicitly observed for the former compared to the latter. This phenomenon is brought about mainly by a higher target voltage in HiPIMS, which makes ionized particles be drawn back by the target itself, thereby resulting in a lower deposition rate [34]. Besides, the decrease of deposition rate in HiPIMS may be contributed by some physical mechanisms [35,36], such as film effect, yield effect, species effect, transport effect and gas rarefaction effect. As can be seen in the case of HiPIMS, deposition rate at -50 V is 64.4 nm/ min, which is slightly higher than that deposited at 0 V (58.6 nm/min). On the contrary, with bias voltage further increasing, the deposition rate continuously decreases from 63.3 nm/min at -100 V, 60.6 nm/min at -150 V to 52.5 nm/min at -200 V.The initial increase in deposition rate could be explained by the fact that more ionized particles are drawn to the substrates under the effect of enhanced electric field in the plasma sheath around the substrate caused by higher bias voltage. The result is consistent with the findings in Fig. 2 where an obvious increase occurs in substrate bias current with increasing bias voltage from 0 V to -50 V. However, by further increasing the bias voltage, a stronger re-sputtering effect and enhanced adatom mobility on the (AlCrTiVZr)N films can be obtained as a result of the enhanced ion bombardment. The former causes a reduction in the number of deposited atoms on the growing films [36], and the latter contributes to the films densification by filling voids between columns or grains, thereby leading to a decrease in



**Fig. 5.** Deposition rates of HiPIMS-deposited (AlCrTiVZr)N films under different bias voltages and the DCMS reference sample.

deposition rate [37].

#### 3.4. Crystal structure identification

Fig. 6 (a) reveals the GIXRD patterns of HiPIMS-deposited (AlCr-TiVZr)N films under different voltages and the DCMS reference sample. Due to a smaller thickness of HiPIMS-deposited films compared to DCMS, the structural information of the WC substrate is also presented in their GIXRD patterns. And the diffraction peaks representing the WC phases increase with increasing bias voltage as the thickness becomes smaller at higher bias voltage. It is clear that only one set of diffraction peaks corresponding to the face-centered cubic (FCC) NaCl-type structure exists in both HiPIMS and DCMS deposited (AlCrTiVZr)N films. Considering the structure and chemical composition of these films, it can be concluded that these (AlCrTiVZr)N films are composed of a single FCC-type nitride instead of a potential mixture of binary nitrides. This phenomenon is mainly attributed to the high-mixing entropy effect of the (AlCrTiVZr)N films which can promote the complete mutual solubility of different elements [38]. For HiPIMS-deposited films, it should be pointed out that the preferred orientation of crystal structure in these films is strongly affected by bias voltage. With increasing the bias voltage from 0 V to -150 V, the intensity of (200) peak is gradually decreased, while the intensity of (111) peak is remarkably enhanced and then becomes the dominant factor at bias voltages of -100 V and -150 V. Usually, the crystal structure evolution in the NaCl -type FCC nitride films is caused by the driving force that can minimize the total energy of films consisting of surface energy and strain energy [39]. Since it has been proved that the (AlCrTiVZr)N films have a NaCl-Type FCC structure, their lowest surface energy plane and the lowest strain energy plane are (200) and (111) [39], respectively. As aforementioned, at higher bias voltage, the energy and flux of ionized particles reaching films will be increased, which enhances the ion bombardment on the growing films, thereby promoting an increase in strain energy. Therefore, the increased strain energy becomes the main driving force to favor the (111) orientation. Increasing the bias voltage further up to -200 V results in a dramatic increase in the (220) intensity and then a shift in the preferred orientation of (AlCrTiVZr)N films from (111) to (220) is obtained. The excessive ion bombardment effect could take place at bias voltage of -200 V, which has a significant negative influence on the (111) orientation during the growth of films. In this situation, the density of collisions, displacements, and thermal spikes in the unit of volume of the (111) orientation reaches its highest level, bringing about the most serious radiation damage [40]. In the FCC NaCl-type structure, the relative number of atom columns per unit area for the [110] and [111] is  $\sqrt{2}$ :  $\sqrt{3}$  [41]. Because of the open structure, (220) orientation is regarded as more open to ion penetration compared with the (111) orientation, which means considerably smaller damages related to atomic collisions as well as the lower sputtering yields in the (220) orientation. This in turn, indicates that as the more open channeling directions, (220) orientation has the highest survival probability and thus can serve as the seed for (AlCrTiVZr)N films growth. Accordingly, a preferred orientation of (220) is presented when the bias voltage is increased further to -200 V.

Debye-Scherrer's formula is utilized to assess the averaged grain size of HiPIMS-deposited (AlCrTiVZr)N films under different bias voltages, as well as the DCMS reference sample. A comparison of average grain size for both techniques is provided in Fig. 6(b). It can be seen that the grain size first decreases gradually to a minimum value around 11.3 nm at -150 V and then increases to 18.8 nm with bias voltage further increasing to -200 V. As bias voltage increases, more ionized particles with higher energy will bombard the growing films, which is beneficial to the increase of defects. On the one hand, it has been reported that defects can prohibit the migration of grain boundaries and thus hinder the growth of individual grain [42]. On the other hand, more defects can promote the increase of preferential nucleation centers [43]. As a result,



Fig. 6. The GIXRD patterns (a) and average grain size (b) of HiPIMS-deposited (AlCrTiVZr)N films under different bias voltages and the DCMS reference sample.

growth from large numbers of such locations can prevent individual grain extension, and results in a decrease in grain size. However, it should be noticed that at higher bias voltage of -200 V, excessive ion bombardment effect is expected to take place, which will give rise to a higher adatom mobility on the growing films, thereby promoting deposited particles to move towards the grain boundaries [43,44]. Consequently, an increasing tendency is observed in the grain size. In addition, for the same reason, it can be seen that a relatively larger grain size is obtained in the (AlCrTiVZr)N films deposited by HiPIMS (H-100) compared to that by DCMS (D-100).

# 3.5. Cross-sectional microstructure and surface morphology

The fractured cross-sectional FE-SEM images of HiPIMS-deposited (AlCrTiVZr)N films under different bias voltages and the DCMS reference sample are illustrated in Fig. 7. As shown in Fig. 7 (f), the DCMS-deposited (AlCrTiVZr)N films (D-100) are characterized by a typical loose columnar-type structure with a visible gap, which grows outward from the substrate surface and then runs through the whole film thickness. By contrast, in Fig. 7(c), the HiPIMS-deposited (AlCrTiVZr)N films (H-100) exhibit a dense and glass-like microstructure even they are

operated under the same deposition conditions as the DCMS reference sample. Interestingly, two different layers separated by a boundary are observed in the cross-sectional microstructures of all HiPIMS-deposited films. Specifically, the upper layer has a columnar crystal structure, while the lower layer has a compact and featureless structure. Our previous work [23] also found such a similar microstructure variation that represented an amorphous structure in the lower layer, which could be explained by the high-mixing entropy, huge film-substrate lattice mismatch, and enhanced ion bombardment effect. Furthermore, as shown in these figures, the microstructure in the upper layer gradually changes from a loose columnar structure (Fig. 7(a)) to denser and finer (Fig. 7(b) and (c)), and even featureless cross-section (Fig. 7(d)), accompanied by a decrease in the thickness of the upper layer when the bias voltage is increased from 0 V to -150 V. However, further increasing bias voltage to 200 V leads to an apparent columnar microstructure again as well as an increase in the thickness of the upper layer. As aforementioned, it is considered that properly increasing the bias voltage can intensify the ion bombardment and enhance the adatom mobility, which will hinder the growth of large columns and force atoms to move into the gaps between columns, thereby promoting the film densification and column refinement [22,45]. However, further



Fig. 7. The cross-sectional morphologies of HiPIMS-deposited (AlCrTiVZr)N films under different bias voltages and the DCMS reference sample.

increasing bias voltage to -200 V causes excessive ion bombardment, which can enhance the migration of small grains to the grain boundaries [46]. Consequently, the formation of columnar structure is as expected at -200 V as shown in Fig. 7 (e).

The three-dimensional topographic AFM images from both HiPIMS and DCMS deposited (AlCrTiVZr)N films are presented in Fig. 8. It is evident that (AlCrTiVZr)N films deposited by HiPIMS present a smoother surface compared to those deposited by DCMS, which is consistent with the conspicuous columnar structure for the DCMS sample in Fig. 7(f). Moreover, the unbiased (AlCrTiVZr)N films exhibit a stalagmite morphology surface with a surface roughness around 1.54 nm. With increasing bias voltage from 0 V to -150 V, the surface of the films is observed to be much smoother and then becomes coarse at a bias voltage of -200 V. It is worth mentioning that at bias voltages of -100 V and -150 V, the films present very smooth surfaces with a roughness of 0.6 nm and 0.4 nm, respectively, and no particular features are observed. This indicates that the moderate bias voltage can make the surface roughness of (AlCrTiVZr)N films smaller than the original surface roughness of Si substrate (about 1 nm). Such evolution of surface roughness is also closely related with the ion bombardment effect, because the enhanced ion bombardment effect at higher bias voltage can promote adatom mobility and the densification of the films [47]. Besides, the increased ion flux and energy of the Ar<sup>+</sup> ion induced by increasing bias voltage also leads to enhanced etching the asperities [48], thus smoothing the surface. However, increasing the bias voltage to -200 V brings about an excessive ion bombardment effect, which can induce the generation of plenty of surface defects to roughen the films surface. As a result, an opposite tendency occurs.

#### 3.6. Mechanical properties

The residual stress of HiPIMS-deposited (AlCrTiVZr)N films under different bias voltages and the DCMS reference sample are displayed in Fig. 9. It should be noted that (AlCrTiVZr)N films deposited by the two techniques suffer from compressive stress, whatever the bias voltage. For the DCMS reference sample, it requires a bias voltage of -100 V to reach the similar residual stress of HiPIMS-deposited (AlCrTiVZr)N films when they are synthesized without bias voltage. In HiPIMS-deposited films, increasing the bias voltage will result in a higher compressive residual stress, increasing from -0.54GPa at 0 V to -3.59GPa at -200 V. It is well known that the residual compressive stress is considered to



Fig. 9. Residual stress of HiPIMS-deposited (AlCrTiVZr)N films under different bias voltages and the DCMS reference sample.

originate from the ion bombardment effect during the PVD process [49]. Specifically, the ionized particles can penetrate deeper into the films and induce the production of defects, such as interstitials, vacancies, dislocations, etc., which expands the lattice and thus brings about the generation of compressive residual stress. Therefore, the higher compressive residual stress in HiPIMS can be attributed to the higher ionization fraction in the HiPIMS compared to DCMS. A more intense ion bombardment effect is as expected in HiPIMS process, which in turn makes the residual stress more compressive. Moreover, since increasing flux and energy of ionized particles can bring about an enhanced ion bombardment effect at higher bias voltage in HiPIMS, it can be concluded that the residual stress is positively related with the bias voltage.

Fig. 10 plots the measured hardness (H) and elastic modulus (E) of HiPIMS-deposited (AlCrTiVZr)N films under different bias voltages and the DCMS reference sample. In terms of HiPIMS, it can be clearly found that the H and E values continuously increase to the maximum value of about 48.3GPa and 497.1GPa, respectively as the bias voltage is



Fig. 8. Three-dimensional topographic AFM images of HiPIMS-deposited (AlCrTiVZr)N films under different bias voltages: (a) 0 V, (b) -50 V, (c) -100 V, (d)-150 V, (e) -200 V, and (f) the DCMS reference sample, -100 V.



Fig. 10. Hardness and modulus of HiPIMS-deposited (AlCrTiVZr)N films under different bias voltages and the DCMS reference sample.

increased to -150 V, whereas further increasing bias voltage to -200 V leads to a slight decrease of H and E values. In above-mentioned sections, the bias voltage exerts a remarkable effect on the crystal microstructure, grain size, cross-sectional morphology, and residual compressive stress of these (AlCrTiVZr)N films. Therefore, this study believes the hardness evolution of these films results from the interaction among these factors. The initial increase in hardness with increasing bias voltage can be explained as follows: (i) Previous studies have established that the FCC nitride films with a preferred orientation of (111) usually exhibit the highest hardness due to the geometrical-strengthening effect [50]. The (111) peak intensity gradually increases and then becomes the dominant one at the bias voltages ranging from 0 V  $\sim$  -150 V (see Fig. 6(a)). In this case, the hardness of films is expected to increase. (ii) A continuous decrease in the grain size from 22.3 nm to 11.3 nm (see Fig. 6(b)) gives rise to a significant grain refinement-strengthening effect. Based on the Hall-Petch effect [51], with the decreasing grain size, the dislocation activity is restricted by grain boundaries and the crack propagation along the grain boundaries is prevented, thereby enhancing the films hardness. (iii) According to the results presented in Fig. 7, the microstructure of (AlCrTiVZr)N films transforms from porous and loose to compact and featureless with the increase of bias voltage. This densification process greatly decreases the voids between columns or grains, which brings about a boundary-strengthening effect [23] and thus contributes to an increase in hardness. (iv) The residual compressive stress shows an increasing tendency with the increase of bias voltage (see Fig. 9). The residual compressive stress, as mentioned above, is induced by the generation of defects that can act as impediments to plastic flow during deformation [52]. It is thus believed that the increase in residual stress is also in favor of the hardening of films. In addition, although the residual stress continuously increases with bias voltage increasing from -150 V to -200 V, an apparent decrease in hardness is observed. The subsequent decrease of hardness at -200 V can be explained by the fact that the shift in the preferred orientation of (AlCrTiVZr)N films from (111) to (220), the increase of grain size up to 18.8 nm as well as the microstructure loosening have weakened the aforesaid geometrical-strengthening effect, refinement-strengthening, and boundary-strengthening effect, respectively.

Additionally, as expected, much higher *H* and *E* values of 35.3GPa and 363.9GPa are obtained for HiPIMS-deposited (AlCrTiVZr)N films (H-100) compared to 25.3 GPa and 329.3 GPa for the DCMS reference sample (D-100). Strangely, it is evident that the preferred orientation of (111) is observed both in Sample H-100 and D-100, and the density of (111) peak is almost the same for them (Fig. 6(a)). Meanwhile, a smaller grain size is obtained in the Sample D-100 compared to H-100 (Fig. 6

(b)). Furthermore, although the Sample H-100 has a higher compressive residual stress, the hardness doesn't exhibit a significant positive correlation with residual stress by comparing Fig. 9 to Fig. 10. Based on the above analysis, it could be deduced that grain size, preferred orientation of (111) and residual stress are not the predominant factors for higher hardness. From the aspect of microstructure, as shown in Fig. 7(c) and (f), Sample H-100 exhibits a dense and glass-like microstructure while Sample D-100 is characterized by a typical loose columnar-type structure. Therefore, in my opinion, the boundary-strengthening effect caused by microstructure densification is the predominant factor for higher hardness in (AlCrTiVZr)N HEAN films system.

#### 4. Conclusions

In the present study, the (AlCrTiVZr)N films were synthesized by HiPIMS using different bias voltages to tune their microstructure and property. Meanwhile, the DCMS deposited (AlCrTiVZr)N films were provided as a reference sample. Results can be concluded as follows:

- (1) Owing to the high-mixing entropy stabilized effect, all (AlCr-TiVZr)N films, either deposited by HiPIMS or DCMS, exhibit a single NaCl-type FCC structure, whatever the bias voltages.
- (2) Compared with DCMS, HiPIMS can offer optical emission lines from all ionized target elements accompanied with a significant increase in intensity, which confirms higher ionization fraction, thereby promoting ion bombardment and adatom mobility. This process is favorable to the structure and property modification for HiPIMS-deposited (AlCrTiVZr)N films. The corresponding predominant strengthening mechanism is mainly attributed to microstructure densification.
- (3) With increasing bias voltage from 0 V to -200 V in HiPIMS, the ion bombardment effect is continuously enhanced, which is attributed to the increasing flux and energy of ionized particles reaching the films. This altered plasma environment has a strong effect on the growth of the (AlCrTiVZr)N films. At a moderate bias voltage of 0 V to -150 V, due to the enhanced ion bombardment effect, the films exhibit a change in the preferred orientation from (200) to (111), a decrease in grain size from 23.3 nm to 11.3 nm and surface roughness from 1.5 nm to 0.4 nm, as well as an increase in residual compressive stress from -0.55GPa to -1.67GPa. Meanwhile, a transformation in cross-sectional morphology from loose columnar structure to dense and featureless structure can also be observed. These changes will bring about geometrical-strengthening effect, refinementstrengthening effect, compressive-strengthening effect, and boundary-strengthening effect, respectively. Consequently, a super-hardness of 48.3GPa can be obtained at -150 V. However, an excessive ion bombardment occurs with further increasing the bias voltage to -200 V, and weakens these strengthening effects even when the residual compressive still increases, which causes a decrease in the hardness.

#### CRediT authorship contribution statement

Yi Xu: Conceptualization, Methodology, Investigation, Writing original draft. Guodong Li: Formal analysis, Writing - review & editing. Guang Li: Validation, Resources. Fangyuan Gao: Supervision. Yuan Xia: Project administration, Funding acquisition.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. Y. Xu et al.

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