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Effect of Pulsing Configuration and Magnetic Balance Degree on Mechanical Properties of CrN Coatings Deposited by Bipolar-HiPIMS onto Floating Substrate

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Abstract: Despite its great potential for thin films deposition and technological applications, the HiPIMS technology has its own limitations including the control of ion energy and flux towards the substrate when coping with the deposition of electrical insulating films and/or the deposition onto insulating/electrically grounded substrates. The bipolar-HiPIMS has been recently developed as a strategy to accelerate the plasma ions towards a growing film maintained at ground potential. In this work, the benefits of bipolar-HiPIMS deposition onto floating or nonconductive substrates are explored. The effect of bipolar-HIPIMS pulsing configuration, magnetic balance-unbalance degree, and substrate's condition on plasma characteristics, microstructure evolution, and mechanical properties of CrN coatings was investigated. During the deposition with a balanced magnetron configuration, a significant ion bombardment effect was detected when short negative pulses and relative long positive pulses were used. XRD analysis and AFM observations revealed significant microstructural changes by increasing the positive pulse duration, which results in an increase in hardness from 7.3 to 16.2 GPa, during deposition on grounded substrates, and from 4.9 to 9.4 GPa during the deposition on floating substrates. The discrepancies between the hardness values of the films deposited on floating substrates and those of the films deposited on grounded substrates become smaller/larger when a type I/type II unbalanced magnetron configuration is used. Their hardness ratio was found to be 0.887, in the first case, and 0.393, in the second one. Advanced application-tailored coatings can be deposited onto floating substrates by using the bipolar-HiPIMS technology if short negative pulses, relative long positive pulses together with type I unbalanced magnetron are concomitantly used.

Keywords: high power impulse magnetron sputtering; bipolar HiPIMS; CrN thin films; ion bombardment; floating substrate

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1. Introduction

In physical vapour deposition (PVD) systems, the control of ion energy and ion-to-neutral flux ratio is essential for optimizing the mechanical properties of the deposited thin films [1]. The nucleation process, densification, phase composition, and microstructure evolution of the growing film are strongly related to the ad-atom mobility, which is significantly affected by the flux and energy of the impinging particles [2]. An appropriate choice of processing parameters, such as pulsing configuration [3], magnetic field topology [4], substrate bias voltage [5,6], and deposition temperature, enables the control of the thermodynamic and kinetic conditions during the growth process. Both microstructure and mechanical properties can be significantly improved by increasing the ad-atom mobility during this process. In general, during PVD process, the ad-atom mobility can be improved by heating the substrate or by applying a substrate bias voltage. Both methods are difficult to be adopted when dealing with the deposition onto temperature-sensitive and electrical non-conductive substrates. More than that, using a high substrate bias is commonly accompanied by the generation of high defect density [7] and high residual stress in the coatings [2].

In the last two decades, due to its energetic ion bombardment, high-power impulse magnetron sputtering (HiPIMS) has become an attractive plasma-based deposition technique to obtain high-quality thin films [8]. In standard HiPIMS configuration, a high negative voltage (of the order of hundreds to thousands of V) is applied to the target in unipolar pulses of few µs to hundreds of µs, with a duty cycle below 10%, leading to pulse target power densities of several kW/cm^2 and a highly efficient ionization of the sputtered material [9,10]. Apart from its high ionization degree, the sputtered material also exhibits a broad ion energy distribution function (IEDF), which increases the average energy of the ion flux. Despite the HiPIMS benefits, the IEDF of sputtered material is still dominated by ions with energies corresponding to the thermalized species [11–13]. While it is common to use a substrate bias to increase the energy of the incoming ion flux, there are often limitations and difficulties in doing this, especially when dealing with deposition of electrical insulating films, deposition onto insulating substrates or when the substrates are electrically grounded. It was thus necessary to develop a new and more effective sputter source, able to control the ion energy and flux towards the substrate, independently on the substrate condition (electrically grounded, biased or floating). A strategy to increase the energy of the ions in a HiPIMS discharge, without applying any substrate bias, has been developed in the last three years [14–16]. Operating the HiPIMS discharge in bipolar mode, where the main short HiPIMS pulse is immediately followed by a positive pulse voltage, results in an efficient ion acceleration process due to a significant increase in the plasma potential [17–19]. The reverse target voltage has an interesting effect within the sputtering processes because it increases the after-glow plasma potential and consequently the incident energy of the ions on the grounded substrate. It was found that the high ionization degree of HiPIMS plasma, combined with an efficient ion acceleration process, may control and enhance the structural and mechanical properties of the growing film [19–21]. The energetic ion irradiation of the growing film during bipolar-HiPIMS provides coating densification and improves its adhesion to the grounded substrate. Our previous investigations, using energy-resolved mass spectrometry during bipolar-HiPIMS discharge operation, revealed a complex IEDF which deviates considerably from the unipolar HiPIMS case. As the plasma potential is very close to the applied reverse target voltage, the outstanding application potential of bipolar-HIPIMS technique resides in its ability to easily control the ion energy and to synthesize advanced metallic coatings onto electrically conductive substrates with no bias. Compared to the standard HiPIMS configuration, the bipolar-HiPIMS yields more compact, denser, smoother, harder, and more adherent coatings due to a much higher energy and flux levels of the film-forming species. Furthermore, the bipolar-HiPIMS has the advantage to easily control the fraction of the accelerated ions [19,22], making it possible to finely tune the properties of the coatings deposited onto grounded substrates [19,20]. One of our most recent works shows that bipolar-HiPIMS enables an energy-enhanced deposition process of high-quality (high hardness, low coefficient of friction, good wear resistance, good adhesion to the substrate, very low surface roughness, and defect free) hydrogen-free DLC thin films on electrically insulated substrates, without using any substrate bias voltage, adhesion interfacial layer or substrate pre-treatment [23]. However, other studies have shown that, apart from reduced arc-generation probability and enhanced discharge stability, there were no net benefits in the case of bipolar-HiPIMS deposition of non-conductive materials [24] or deposition onto nonconductive or floating substrates [25]. The apparently contradictory results, in terms of the effect of positive target voltage on the film's properties, reported in the literature, could be due to some different deposition conditions and/or deposition systems used (e.g., different pulsing and/or magnetic field configurations). The influence of pulsing configuration on the fraction of accelerated ions towards a grounded mass spectrometer was recently reported by Viloan et al. [22]. According to their work, the fraction of ions, accelerated to energies corresponding to the full positive target potential, is close to 100% when the duration of the negative and positive pulses is properly selected. For negative pulse duration shorter than 20 μs and positive pulse duration longer than 50 μs, almost all plasma ions are accelerated during the bipolar-HiPIMS operation. This finding results from the fact that plasma ions are accelerated only during the positive pulse. If the negative pulse duration is too long, most of the plasma ions arrive at the substrate during the negative pulse and only a small fraction of them will gain energy from the high plasma potential reached during the positive pulse. If the positive pulse duration is too short, only a small fraction of ions will gain extra energy from the plasma potential, most of them arriving at the substrate without being accelerated. Otherwise, if the positive pulse is too long, a second discharge may develop during the positive pulse, as was suggested by Hippler et al. [26,27] and demonstrated by Kozák et al. [28].

During bipolar-HiPIMS deposition of metal coatings onto grounded substrates, it was found that the accelerated ions gain some energy, roughly corresponding to the reverse target potential and most of the ion acceleration process happens at the substrate sheath. When a floating substrate is in contact with the plasma, it will be charged with electrons reaching a certain floating potential. In this case, the accelerated ions will gain energy corresponding only to the difference between the plasma and floating potential ($E_{cin} = E_0 + qe(V_{pl} - V_{fl})$). As the plasma parameters are time dependent, the space-and-time floating and plasma potential distributions are strongly related to the pulsing and magnetic field configurations. Therefore, during bipolar-HiPIMS deposition onto nonconductive substrates, apart from the proper selection of pulsing configuration, a better selection of the magnetic field configuration is needed to get the maximum benefit from this technique. There is a lack of information in the literature regarding the influence of the magnetic field configuration on the ion acceleration mechanism during the bipolar-HiPIMS operation. It is very difficult to draw a conclusion regarding the benefits of the bipolar-HiPIMS technique since for the already reported data, both pulsing and magnetic field configurations were varied to a large extent.

The aim of this work is to find the optimum pulsing and magnetic field configurations in order to gain maximum benefits of high plasma potential during bipolar-HiPIMS deposition onto floating or nonconductive substrate. We have studied the effect of bipolar-HIPIMS pulsing and magnetic configurations and substrate condition (floating or grounded) on both plasma characteristics and microstructural and mechanical properties of chromium nitride (CrN) films. CrN was chosen as a model system due to the limited reactivity of Cr towards nitrogen, which allows a better control of film stoichiometry when different pulsing and magnetic field configuration are used. In addition, CrN films are well known for their attractive properties like high hardness, good wear and corrosion resistance [29], and thermal stability [30], and it is commonly used as a protective material for alloys servicing in high temperature and corrosive environments. Since the mechanical properties of films are mainly influenced by their chemical composition, microstructure (texture, packing density, grain size), morphology, and residual stress, in this work, great attention was given to the interrelation between microstructure, morphology, and resulting mechanical properties of the CrN films. X-ray diffraction (XRD) analysis, cross-sectional scanning microscopy (SEM), atomic force microscopy (AFM), and nanohardness tests were used to explore the effects of growth conditions on the microstructural evolution of CrN thin films deposited by reactive bipolar-HiPIMS. Space-and-time plasma and floating potential distributions allow to explain the ion acceleration mechanism. We showed in this work how the microstructure and mechanical properties of the CrN films deposited onto the floating substrate can be effectively controlled by properly selecting the pulsing and magnetic field configurations.

2. Materials and Methods

2.1. Films Deposition

In this work, nanocrystalline CrN thin films (thickness of about 400 nm) were deposited by bipolar-HiPIMS on silicon (Si) substrates using different pulsing and magnetic configurations in order to investigate the effects of ion bombardment on the microstructure evolution and films' properties. The experiments were performed in a custom-built cylindrical sputtering system device (40 cm in diameter, 40 cm in height), using a homemade bipolar-HiPIMS power supply. The schematic description of the deposition system and bipolar-HiPIMS power supply can be found in our previous paper [19].

CrN thin films were deposited via reactive sputtering of a chromium target (99.99% purity, 50 mm in diameter) in an argon–nitrogen gas mixture (flow ratio 1:1) using a circular 2-inch balanced magnetron (TORUS 2″ from Kurt J. Lesker, Pittsburgh, PA, USA). In order to understand the effect of ion bombardment on the microstructural and mechanical properties, the films were deposited onto Si p-type (100) substrates, without external heating. A base pressure below 10^{-4} Pa was reached prior to all depositions using a turbo-molecular pump backed by a dry-scroll pump. During the deposition process, the gas mixture pressure was set to 1 Pa by throttling the separation valve. Using a negative pulse (pw_{-}) of 5 µs and a voltage amplitude (U_{-}) of −800 V, a peak target current of 35 A was reached. The voltage amplitude of the positive pulse (U_{+}) was set to +230 V and no delay between the negative and positive pulses was used. The average power was maintained constant at 100 W by a proper selection of the repetition frequency. The substrate was positioned 10 cm away from the target surface (facing the centre of the target). During the deposition process, the substrate could be either electrically grounded or floating (self-biased) by connecting or disconnecting the substrate holder from ground. No substrate treatments were performed prior to or during the deposition.

In order to investigate the effect of the magnetic field configuration on plasma characteristics and films' properties, an external magnetic coil was used. The magnetic balance-unbalance degree was changed from balanced to unbalanced type I or type II, according to the classification made by Window and Savvides [31], by properly biasing the coil. Thus, the magnetic flux density was varied between −180 and +180 G in the target's surface region (weakening or strengthening the magnetic flux through the face of the outer magnetron pole) to simulate a magnetically unbalanced type I or type II configuration. Within this range, the peak ion density at the substrate was changed between 1.5 and 15.0 mA/cm^2. The gas ratio, total working pressure, target-to-substrate distance, deposition time, negative target voltage, and average power were maintained constant during all depositions. The temporal evolution and the axial distribution of the plasma and floating potential were monitored using an emissive/cold probe. More details on the emissive probe measurements can be found elsewhere [32]. Figure 1 shows the schematic diagram of the experimental set-up used in this work.

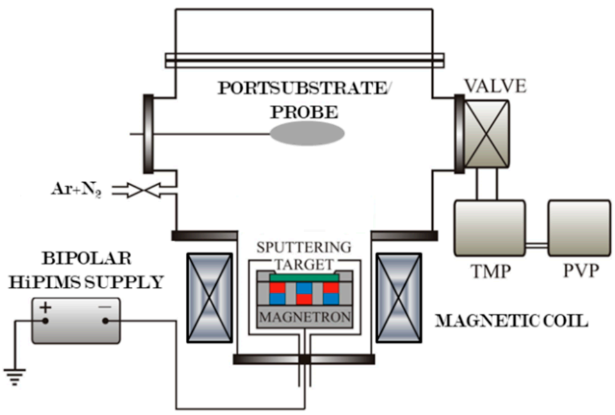

Figure 1. Schematic diagram of the experimental set-up.

2.2. Films Characterization

The structural and phase analyses of the deposited films were conducted using X-ray diffraction (XRD), in Bragg–Brentano configuration, and a Shimadzu LabX XRD-6000 diffractometer (supplied by Shimadzu Corporation, Kyoto, Japan), equipped with a CuK_α radiation source (λ = 1.54059 Å). The morphology and roughness of the films were investigated by atomic force microscopy (AFM,), using a SolverPro system from NT-MDT(Moscow, Russia) and the Nova software (version 1.0.26.1443 from NT-MDT). To eliminate the influence of substrate topography on the coatings' surface roughness, the CrN thin films were deposited onto mirror-like polished Si wafers. Si substrate allows to easily fracture the samples and to prepare them for cross-sectional electron microscopy investigations. Microstructure observations of all the samples were carried out using scanning electron microscopy (SEM). Cross-sectional SEM images and thickness measurements were performed using a field emission scanning electron microscope (Hitachi S-3400N, Hitachi Science Systems, Tokyo, Japan). The chemical composition was accurately measured by energy dispersive X-ray spectroscopy (EDX) using a Neon 40 EsB SEM microscope from Carl Zeiss GmbH. The mechanical parameters (hardness, *H*, Young's modulus, *E*) were investigated by nanoindentation tests, in ambient atmosphere, using a Nanoindentation Tester (NHT^2, equipped with a three-sided diamond pyramidal Berkovich indenter tip, tip radius of about 100 nm) from CSM Instruments (CSM Instruments, Peseux, Switzerland). The values for *H* and *E* were obtained by analysing the loading and unloading segments of the indentation curves, according to the Oliver–Pharr method. In order to minimize the substrate's influence on the indentation data, the indentation depth was kept below 40 nm (10% of the films' thickness).

3. Results and Discussion

3.1. Control of CrN Thin Film Properties by Pulsing Configuration

3.1.1. Sputtering Condition. Pulse Duration Selection

Previous studies have shown that the fraction of accelerated ions during bipolar-HiPIMS strongly depends on the pulsing configuration [22]. During bipolar-HiPIMS, the fraction of accelerated ions can be accurately controlled by keeping constant the duration of negative pulse and by varying the duration of the positive pulse. The selection of the positive pulse duration appears thus as an interesting approach to control the ion bombardment without changing the parameters of the plasma generated during the main negative HiPIMS pulse. Since bipolar-HiPIMS is an intermittent discharge, special attention to the transient property of the plasma dynamics and kinetics must be paid. Thus, the space-and-time plasma and floating potential distribution measurements can help us to understand the ion acceleration mechanism during deposition on the floating substrate. Figure 2 shows the influence of the negative pulse duration on the plasma and floating potential measured at the substrate position (10 cm away from the target) during bipolar-HiPIMS of a Cr target using a balanced magnetron. The positive pulse duration (pw_+) was set to 30 μs, while the amplitude of the negative and positive pulses were −800 V and +230 V, respectively. As can be seen, for short negative pulses, during the reverse pulse, the plasma potential is almost constant and reach values close to the target voltage. It should be noted that the plasma potential during the positive pulse is quasi-uniformly distributed along the target-to-substrate distance, a similar observation being recently reported elsewhere [17,32]. This means that during deposition onto grounded substrate, the plasma ions are accelerated only in the substrate sheath potential. For long negative pulses, the small gap in the plasma potential waveforms (visible for negative pulses of 15 and 20 μs) indicates the occurrence of a second discharge [28]. The emissive probe measurements (results not shown here) performed along the discharge axis, at different distances from the target (5–140 mm), confirmed a uniform axial distribution of the plasma potential during the reverse pulse (as outlined in Figure 2a), with a plasma potential value very close to the reverse target voltage.

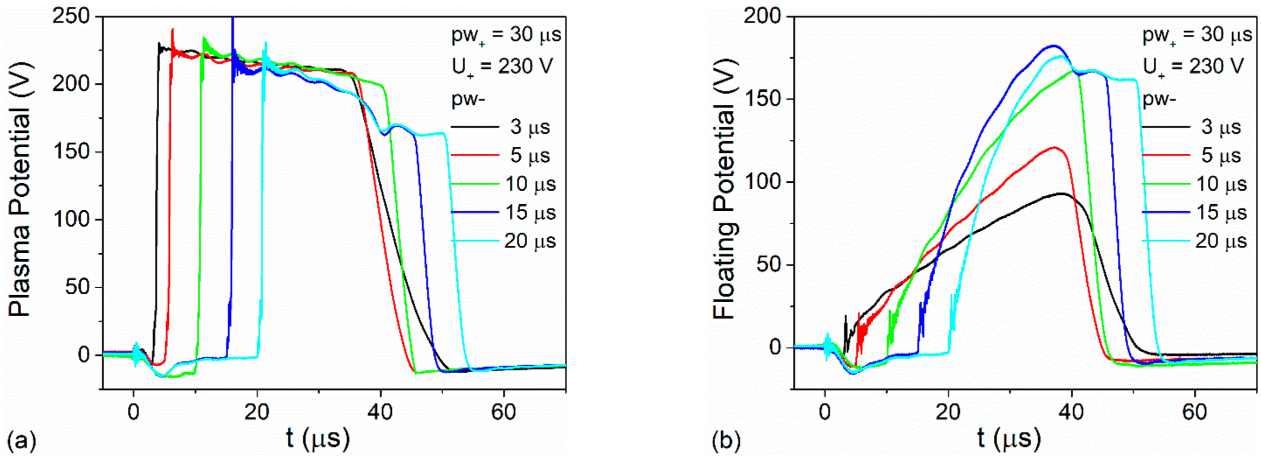

Figure 2. Temporal evolution of plasma potential (**a**) and floating potential (**b**) during bipolar-HiPIMS operation with $U_{-} = -800$ V, $U_{+} = 230$ V, $pw_{+} = 30$ μs and different negative pulses.

Contrarily to the plasma potential waveforms, the temporal evolution of floating potential measured by cold probe (unheated emissive probe) at the substrate position using different negative pulses shows a different temporal evolution. The floating potential increases during the positive pulse and, as the negative pulse increases, its peak approaches the plasma potential value. During the positive pulse, the target absorbs electrons and repels positive ions [15]. Since the electrons' mobility is much higher, a significant difference between plasma and floating potentials appears at the beginning of the positive pulse. As long as the floating potential is maintained low, the increase of plasma potential results in an efficient ion-acceleration towards the floating substrate.

Decreasing the duration of the negative pulse, a clear decrease in the peak floating potential was observed. The reduction of the peak floating potential for shorter negative pulses may be ascribed to the suppression of the charging rate of a floating substrate due to a low ion flux towards the substrate. When the substrate is floating or nonconductive, the ions gain energy only from the potential fall given by the difference between plasma potential and floating potential of the substrate. Therefore, the difference between plasma potential and floating potential gives more valuable information on the ion acceleration mechanism and ion energy gain during the reverse pulse, showing how efficient the ion acceleration towards a floating substrate is. Figure 3 illustrates the influence of negative pulse duration on the difference between the plasma and floating potentials.

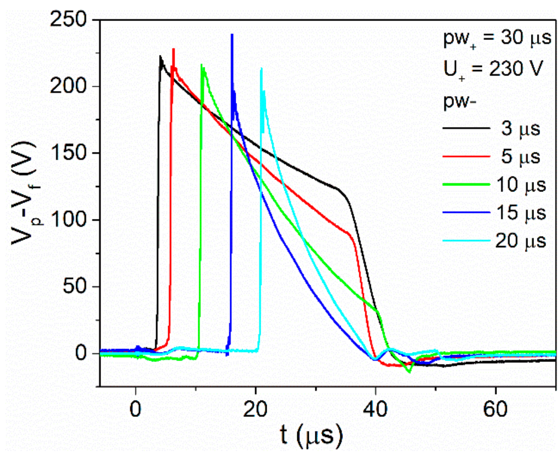

Figure 3. Difference between the plasma and floating potentials during bipolar-HiPIMS operation with $U_{-} = -800$ V, $U_{+} = 230$ V, $pw_{+} = 30$ μs and different negative pulses.

This image clearly shows that as the negative pulse increases, the energy gained by the ions during the reverse pulse is lower. The ions gain energy corresponding approximately to the target potential only at the beginning of the reverse pulse, which means that the ion acceleration efficiency gradually decreases during the positive pulse. In contrast to the axial distribution of the plasma potential, which is constant along the target-to-substrate distance, the axial distribution of the floating potential varies and its distribution is strongly affected by the negative pulse duration. As the negative pulse duration increases, the floating potential approaches the plasma potential and the efficiency of ion acceleration decreases. Figure 4 shows the axial distributions of the floating potential and the difference between plasma and floating potential for different negative pulses, measured at 10 µs after the onset of the positive pulse. Based on the results presented in Figure 4, it can be noticed that the ion acceleration mechanism during the bipolar-HiPIMS deposition on floating substrate is more efficient when the discharge operates with short negative pulses. Therefore, we decided to set the negative pulse to 5 µs and to investigate the influence of the positive pulse duration on both ion energy and CrN films' properties. The influence of the ion energy on the crystallographic structure and microstructure of the deposited CrN films is discussed in the next subsection.

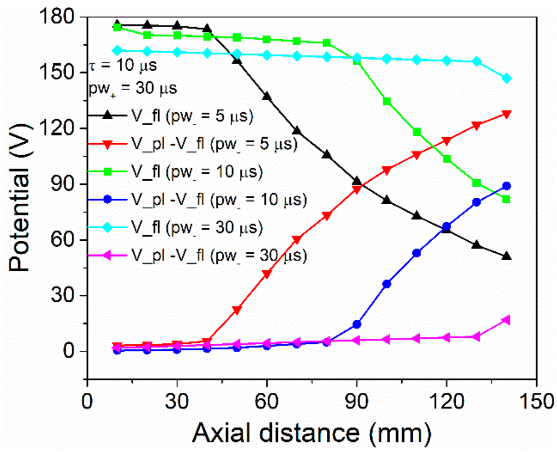

Figure 4. Axial distributions of the floating potential and difference between plasma and floating potential, measured at 10 µs after the positive pulse during bipolar-HiPIMS with $U_{-} = -800$ V, $U_{+} = 230$ V, $pw_{+} = 30$ µs, and negative pulses of 5, 10, and 30 µs.

3.1.2. Phase Composition and Microstructure

The chemical composition of the deposited films, measured by EDX, revealed that all the samples presented in this study have near-stoichiometric composition with (51 ± 2) at.% Cr and (49 ± 2) at.% N. Therefore, it can be concluded that the phase composition, microstructure and mechanical properties of the CrN thin films are not influenced by the chemical composition. The effect of pulsing configuration and substrate's condition on the crystal orientation was studied by XRD. Figure 5 shows XRD patterns and crystallite size (corresponding to (111) and (200) crystallographic phase) of CrN thin films prepared by bipolar-HiPIMS on grounded and floating substrates, using a magnetically balanced magnetron and different positive pulse durations. The negative pulse duration was set to 5 µs, while the amplitudes of negative and positive pulses were −800 V and +230 V, respectively. The XRD measurements revealed that all the samples exhibit a polycrystalline structure whose texture is strongly affected by the positive pulse duration. It can be seen that a large shift towards lower Bragg's diffraction angles as compared to that of the bulk target material appears in the case of CrN film deposited onto grounded substrate by bipolar-HiPIMS with long positive pulses. The larger shift of the diffraction peaks in CrN films deposited by bipolar-HiPIMS onto grounded Si substrate is attributed to their higher compressive residual stress, which was probably generated by the energetic ion bombardment during the positive pulse.

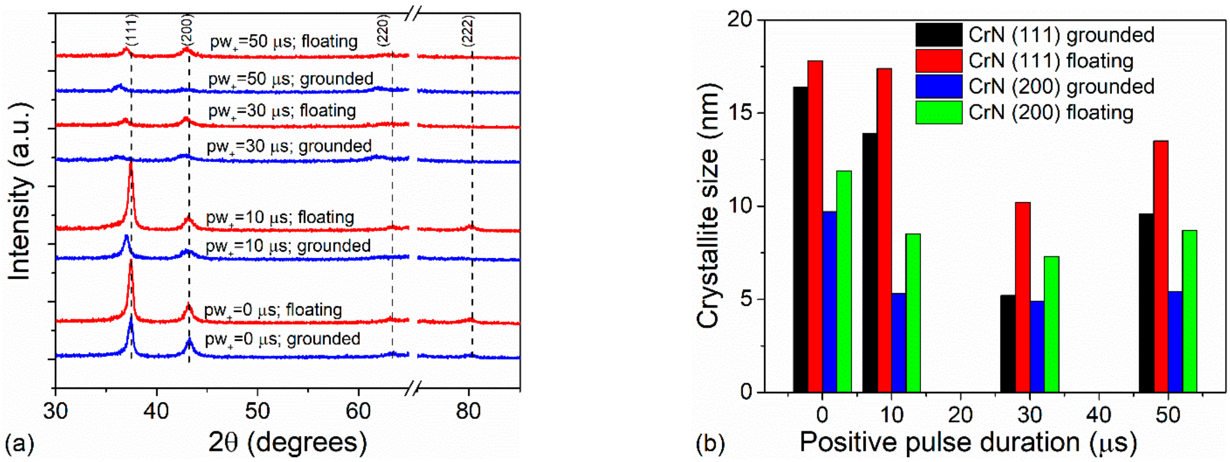

Figure 5. XRD patterns (**a**) and crystallite size (**b**) of CrN thin films deposited by bipolar-HiPIMS on grounded and floating substrate using $U_{-} = -800$ V, $U_{+} = 230$ V, $pw_{-} = 5$ μs, and positive pulse (pw_{+}) durations of 0, 10, 30, and 50 μs.

The XRD measurements revealed that the CrN films deposited by HiPIMS and BP-HiPMS with balanced magnetic field exhibited a crystal structure with strong (111) and weak (200), (220), and (222) orientations. The preferential orientation growth is determined by the least total energy resulting from the competition between strain and surface energy. If the strain energy is dominant, cubic nitrides grow with texture on (111) plane, which has less surface energy and higher atom density. If the surface energy is dominant, then the texture will be on (200) plane, which has higher surface energy [33]. The texture of CrN samples prepared by conventional HiPIMS on grounded or floating substrate is comparable to that of those prepared by bipolar-HiPIMS with short positive pulses. Nevertheless, the intensities of the peaks decrease when the films grow on grounded substrates and/or are deposited in bipolar-HiPIMS with long positive pulses, indicating a low crystallinity and an incomplete crystal structure. The intense ion bombardment which takes place during positive pulse leads to a nanocrystalline structure.

The crystallite size (t) of the deposited films was estimated using the Scherrer equation [34]:

$$t = \frac{0.9\lambda}{\beta_{\frac{1}{2}} \cos\theta}$$

where λ is the wavelength of the CuK_{α} X-Ray source and $\beta_{\frac{1}{2}}$ is the broadening of the diffraction line (FWHM-full width at half its maximum intensity). The XRD peak broadening was determined by fitting the two most intense diffraction lines ((111) and (200)) with a Pseudo-Voigt profile function. As compared to the samples deposited on floating substrate, those deposited onto grounded substrate have much smaller crystallites. This could be attributed to the more energetic ion bombardment which breaks the crystallite growth. The kinetic energy transferred from the ions to the ad-atoms on the substrate will increase the ad-atom mobility and diffusivity, generating a large number of nucleation sites and decreasing the grain size [35]. The ad-atoms can move or diffuse into the inter-grain voids providing more compaction of the coatings. Peaks positions and grain sizes for films deposited either on floating or grounded substrates are essentially affected by variations of the positive pulse duration indicating a change in the bombarding conditions with the duration of the positive pulses. The results show that even the films deposited on floating substrates are subjected to an increasing ion bombardment with an increase in positive pulse duration. By increasing the duration of the positive pulse, the fraction of the accelerated ions in the difference of plasma and floating potentials increases too, leading to an energy-enhanced deposition process.

The effect of the pulsing and magnetic field configurations on the films' topography was investigated by atomic force microscopy. Changing the pulsing and magnetic field configuration, no significant changes in the surface topography were observed, therefore

AFM topography images are not presented here. All the samples exhibit a granular topography with very fine grains distributed evenly on their surface. Figure 6 shows that all the films deposited on grounded substrate exhibit very low surface roughness, with an average value close to 1 nm, irrespective of the reverse pulse duration. This could be attributed to the intense and energetic ion bombardment which enhances the ad-atom mobility and provide a very smooth surface. Increasing the duration of the positive pulse, the surface roughness of the films deposited on floating substrate gradually increases from 1.3 nm to 2.3 nm. It seems that a larger fraction of accelerated ions leads to a slight increase of the surface roughness.

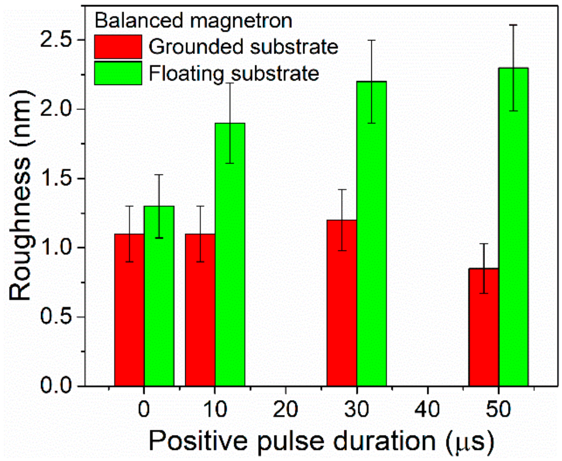

Figure 6. Average roughness of CrN thin films prepared by BP-HiPIMS on grounded and floating substrate using $U_{-} = -800$ V, $U_{+} = 230$ V, $pw_{-} = 5$ μs and positive pulse durations of 0, 10, 30, and 50 μs.

3.1.3. Mechanical Properties

During the deposition process with a balanced magnetron, the hardness gradually increases as the positive pulse duration increases, suggesting that the films were subjected to an enhanced ion bombardment during their growth. Figure 7 indicates that the average values of hardness ranged between 5 and 16 GPa. Similar ranges of values were reported in the case of CrN coatings synthesized by dual-HiPIMS on floating substrates [36] and by HiPIMS on grounded substrates [37]. The films deposited onto grounded substrates exhibit the higher hardness due to a more energetic ion bombardment, in this case, the positive ions being accelerated during the reverse pulse to energy corresponding approximately to the applied reverse target potential. Figure 7a shows that the hardness is highly sensitive to the reverse pulse duration, irrespective of the substrate condition. Increasing the fraction of the accelerated ions, by increasing the positive pulse duration, the hardness is significantly improved, even in the case of films deposited on floating substrates, indicating an enhanced ion bombardment. The enhanced ion bombardment could lead to higher intrinsic compressive stress and more densification of the films. This densification is an indication of enhanced ad-atom mobility due to a more efficient momentum transfer to the ad-atoms from a higher fraction of accelerated ions [38]. On the other hand, the higher hardness found for the films deposited on grounded substrates may be also due to grain refinement (see Figure 5b), which increases the grain boundaries and creates more obstacles to dislocation motion [39]. The hardness to Young's modulus ratio is a good indicator of the resistance against elastic strain to failure and it is commonly used to predict the wear resistance. Young's modulus of CrN films deposited on floating substrates increases with the positive pulse duration and consequently, the H/E ratio follows the same trend as hardness (Figure 7b). The enhancement of the mechanical performances of the films deposited on floating substrates is attributed to an increased fraction of accelerated ions as a result of an increase in the positive pulse duration. This means that an enhanced ion acceleration process occurs during the reverse pulse and its efficiency is closely related to the pulsing configuration.

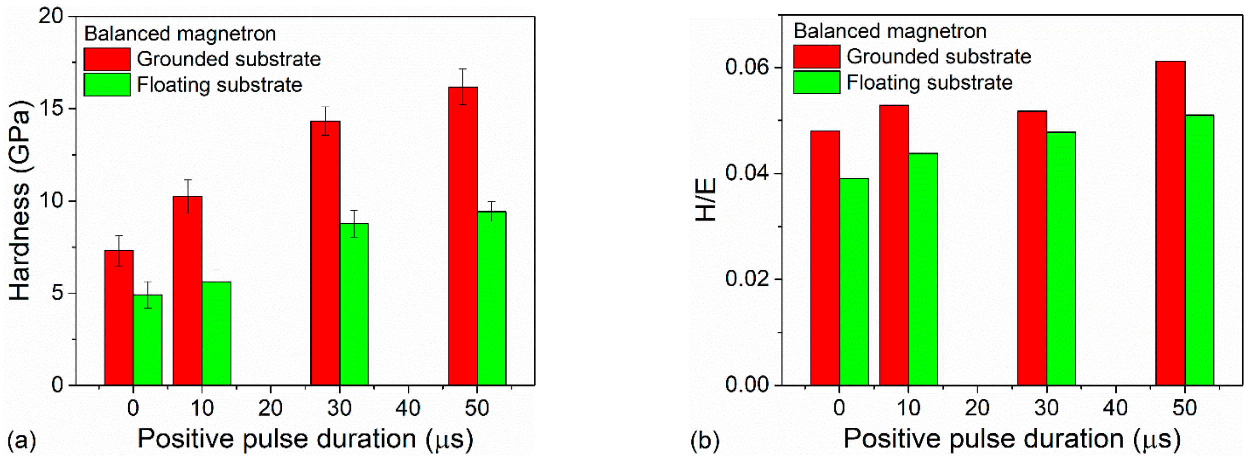

Figure 7. Hardness (**a**) and H/E ratio (**b**) of CrN thin films prepared by bipolar-HiPIMS on grounded and floating substrate using U_{-} = −800 V, U_{+} = 230 V, pw_{-} = 5 μs and positive pulse durations of 0, 10, 30, and 50 μs.

All these results indicate a clear effect of the ion bombardment even in the case of CrN films deposited onto floating substrates. The benefits of bipolar-HiPIMS to control the ion flux and energy towards a floating substrate become clear since the mechanical properties of the films are significantly improved.

3.2. Control of CrN Thin Film Properties by Magnetic Field Configuration

3.2.1. Sputtering Condition. Magnetic Balance Selection

Based on the above presented results, CrN films were deposited by bipolar-HiPIMS on grounded and floating substrates using different magnetic field configurations. The following set of process parameters was used: pw_{-} = 5 μs, pw_{+} = 30 μs; U_{-} = 800 V, U_{+} = 230 V, f = 3 kHz, p = 1 Pa, B = 0/−180/+180 G. The magnetic configuration was changed to simulate an unbalanced magnetron type I by properly biasing the magnetic coil (B = 180 G). In this case, as the magnetic flux density increases, the floating potential decreases, while the plasma potential waveforms remain unchanged. Figure 8 shows the influence of the external magnetic flux density on the temporal evolution of the plasma potential and floating potential.

When the magnetic balance of the magnetron was changed to simulate a discharge with an unbalanced magnetron type II, the external magnetic field seems to have an opposite effect on the temporal evolution of the floating potential compared to the case with an unbalanced magnetron type I (Figure 9). As the external magnetic flux density increases, the plasma potential remains unchanged and the floating potential during positive pulse increases. For high levels of the magnetic flux density, the positive charge collected by the probe will increase its potential up to a value close to the plasma potential. In this case, when a magnetically unbalanced type II magnetron source is simulated, the floating potential quickly approaches plasma potential, their time evolutions having roughly similar trends. This is consistent with the data reported by Pajdarova et al. [40], who showed that during bipolar-HiPIMS discharge, with an unbalanced magnetron type II configuration, the plasma potential and the floating potential waveforms behave roughly in the same manner. It seems that the magnetic field has a critical effect on the electron trapping near the cathode, being a key factor in controlling the ion current towards the substrate and the charging rate of a floating substrate. The diffusion loss of after-glow plasma is much faster during the sputtering process using a magnetically unbalanced type II magnetron as compared to a magnetically unbalanced type I.

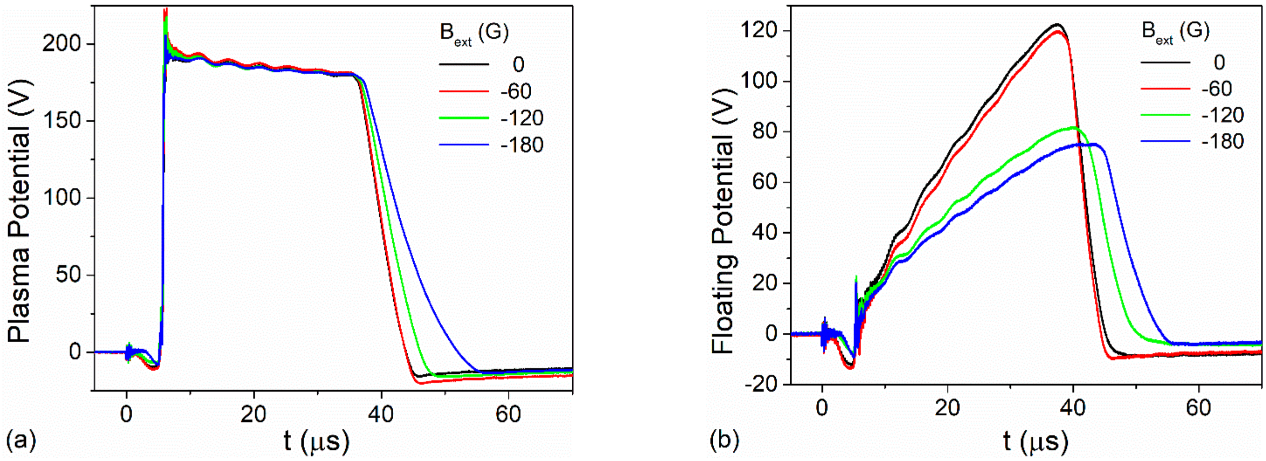

Figure 8. Temporal evolution of plasma potential (**a**) and floating potential (**b**) measured at the substrate position during bipolar-HiPIMS discharge with $U_{-} = -800$ V, $U_{+} = 230$ V, $pw_{-} = 5$ μs, $pw_{+} = 30$ μs and different magnetic flux densities.

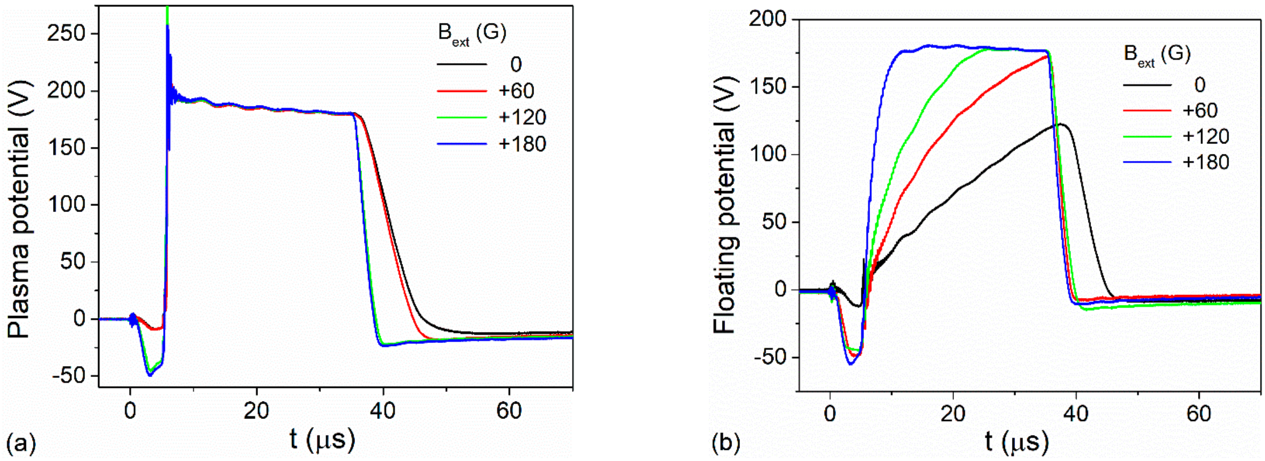

Figure 9. Temporal evolution of plasma potential (**a**) and floating potential (**b**) during bipolar-HiPIMS discharge with $U_{-} = -800$ V, $U_{+} = 230$ V, $pw_{-} = 5$ μs, $pw_{+} = 30$ μs and different external magnetic flux densities.

The influence of the magnetic configuration on the ion acceleration mechanism towards a floating substrate is illustrated in Figure 10. Simulating an unbalanced magnetron type II, it was found that there is a very short time of ion-acceleration immediately after applying the reverse pulse, while for an unbalanced magnetron type I, the acceleration voltage is close to the applied target voltage at the beginning of the reverse voltage and it slowly decreases during the reversed pulse. The faster charging rate during bipolar-HiPIMS with an unbalanced magnetron type II is due to a faster diffusion loss of after-glow plasma and due to the higher current density towards the substrate (note that the current density during the sputtering process with an unbalanced magnetron type II is 10 times higher than that found with an unbalanced magnetron type I). When an unbalanced type II magnetic field configuration is simulated, the plasma is more extended to the substrate and the transport of charge carriers from the target to the substrate is not significantly impeded by the magnetic field lines. This is consistent with the results reported by Pajdarova et al. [40] who show similar behaviour of V_p–V_f at the beginning of the reverse pulse using an unbalanced type II magnetic field configuration.

The estimated ion-accelerating voltage (V_p–V_f) during the positive reversed pulse presented in Figure 10 is also consistent with the data reported recently by Du et al. [24], who simulated the efficiency of the ion bombardment process during bipolar-HiPIMS deposition on metallic substrates covered by a dielectric film with different thicknesses (capacitances). They showed that for a dielectric film with high capacitance to ground (small thickness), the substrate floating potential remains close to the ground potential during the entire positive HiPIMS pulse and the ion acceleration efficiency is very high, while if the dielectric film has low capacitance (large thickness), the floating potential of the substrate quickly attains the plasma potential and the ion acceleration efficiency is very low. This scenario approaches very well the experimental data presented in Figure 10, illustrating the influence of the magnetic field configuration on the ion acceleration efficiency. Therefore, the efficiency of ion acceleration towards a floating substrate is high for an unbalanced magnetron type I and very low for the type II one.

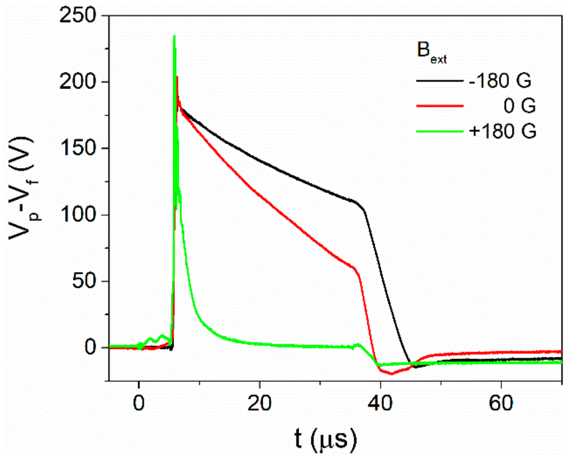

Figure 10. Influence of the magnetic balance degree on the difference between the plasma and floating potentials during bipolar-HiPIMS discharge with U_- = −800 V, U_+ = 230 V, pw_- = 5 μs, pw_+ = 30 μs.

3.2.2. Phase Composition and Microstructure

Figure 11 shows the influence of the magnetic field configuration on the crystallographic structure and grain size of CrN films deposited on grounded and floating Si substrates.

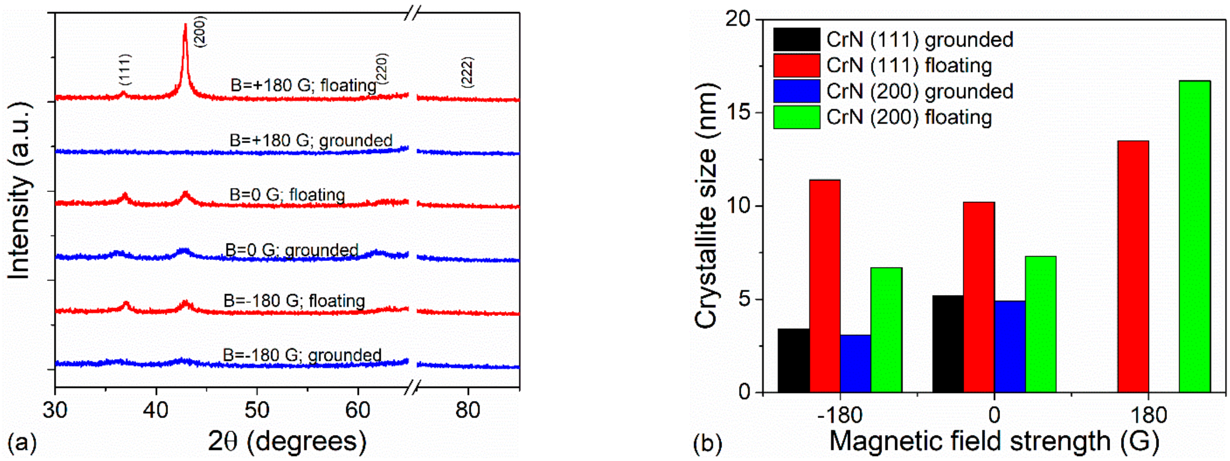

Figure 11. XRD patterns (**a**) and crystallite size (**b**) of CrN thin films prepared by bipolar-HiPIMS on grounded and floating substrate using U_- = −800 V, U_+ = 230 V, pw_- = 5 μs, pw_+ = 30 μs and different magnetic field configurations.

Changing the magnetic balance degree from balanced (B = 0 G) to unbalanced type II (B = +180 G), the ion flux significantly increases and causes a change from a preferred (111) orientation to a pronounced (200) orientation during the deposition on floating substrates. The high ion flux ratio characterized by low energy, provided by the unbalanced type II magnetron sputtering on floating substrates, causes an enhanced diffusion capacity of the absorbed atoms which allows the formation of an intense (200) texture. This is in agreement with previous studies showing that an enhanced low energy ion bombardment at the substrate leads to a different mechanism of ad-atom diffusion, providing a preferential (200) phase orientation [2,41]. On the other hand, the bipolar-HiPIMS deposition with unbalanced type II magnetic field on grounded substrates leads to an amorphous to nanocrystalline structure of CrN films. The high ion flux together with the increased ion energy at the substrate, due to an efficient ion acceleration (ions gain energy corresponding roughly to reverse target potential), lead to a higher mobility of the ad-atoms, which in turn, will fill the voids between the grains and break the columnar growth, creating new nucleating sites. The smaller grains, with an average size below ~15 nm, in the CrN single layers, reflect the high density of nucleation sites on the Si surface in the early stages of the film growth process. The grain growth is hindered by the ion-irradiation induced re-nucleation; thus, a recrystallization and a refinement of grains occur. The drawback of using a high ion energy and a high ion flux by using bipolar-HiPIMS (with high positive target voltage), grounded substrates and an unbalanced magnetron (type II) is the generation of high residual stresses and high defect densities in the Cr films.

The effect of the magnetic field configuration on CrN films microstructure is presented in Figure 12. The morphology of the fractured films deposited onto floating Si substrates, using an unbalanced type II magnetron configuration (external magnetic flux density B = +180 G), indicates an intergranular fracture along the columnar grains due to the low film densification and weak boundary bonding strength between the grains. The film shows a porous columnar structure with long columnar grains and clear grain boundaries throughout the film thickness. The columnar microstructure is caused by the low energy ion bombardment, as shown in Figure 10, indicating that during the bipolar-HiPIMS with an unbalanced magnetic degree type II, the plasma ions are accelerated only for a very short period of time, at the beginning of the positive pulse.

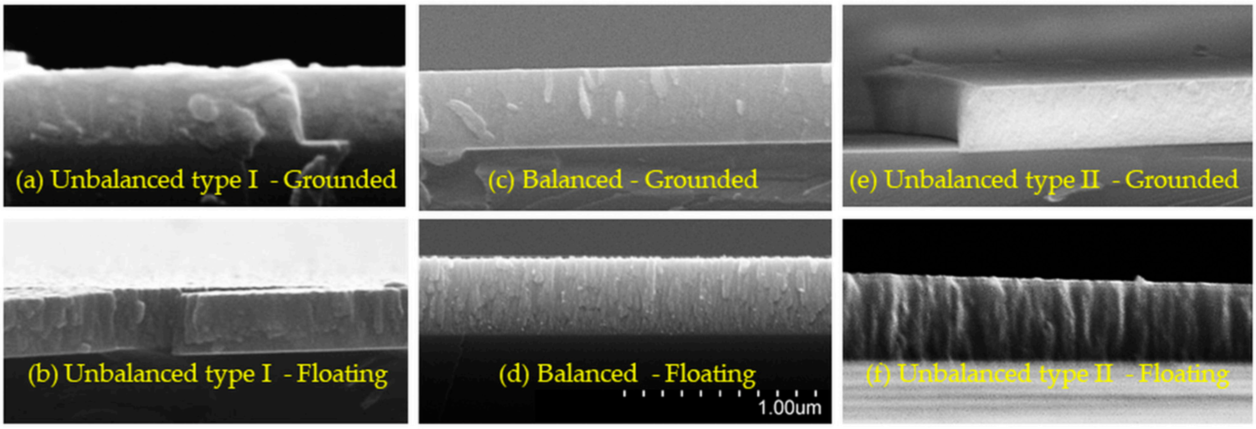

Figure 12. Cross-sectional SEM images of CrN thin films prepared by bipolar-HiPIMS on grounded and floating substrates using U_{-} = −800 V, U_{+} = 230 V, pw_{-} = 5 µs, pw_{+} = 30 µs and different magnetic field configurations. The scale bar shown in Figure 12d corresponds to all SEM images.

As the magnetic balance-unbalance degree is changed from unbalanced magnetron type II to unbalanced type I, the microstructure of the films deposited on floating substrate changes from a columnar microstructure to a compact and dense microstructure without inter-columnar voids. It can be seen that the column boundaries of the films deposited in unbalanced magnetron type II configuration are well defined, while the boundaries of the films deposited in unbalanced magnetron type II configuration are fuzzy, indicating a more compact structure.

During the deposition on grounded substrates, the energetic ion bombardment is very high, irrespective of the magnetic balance-unbalance degree, and this leads to a higher mobility of the ad-atoms, which in turn will fill the voids between grains and it will break the columnar growth, leading to a more compact structure.

CrN film deposited onto grounded Si substrate using a magnetically unbalanced type II configuration (B = +180 G) shows a featureless microstructure and this could be attributed to a much higher ion energy and flux towards the substrate.

The influence of the magnetic configuration on the surface roughness is presented in Figure 13. When CrN thin films were deposited on grounded substrates using an unbalanced magnetic field type II, the average roughness significantly decreased down to 0.25 nm. This is in good agreement with the SEM image which showed a featureless microstructure (Figure 12). The high ion energy and high bombarding ion flux seem to be responsible for the roughness drop and film densification. It is not excluded that a re-sputtering process takes place during the positive pulse, leading to the removal of asperities from the surface of the growing film. The effect of magnetic balance configuration on the surface roughness is visible when the films are deposited onto floating substrates. By changing the magnetic unbalance degree from type I ($B = -180$ G) to type II (B = +180 G), the surface roughness gradually decreases from 2.5 to 0.8 nm. The increased ion flux with low energy leads to lower surface roughness.

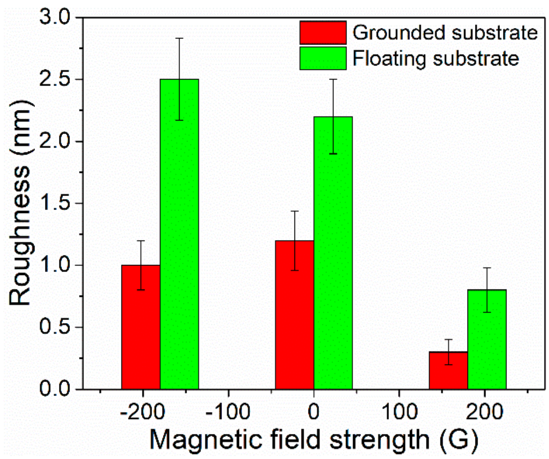

Figure 13. Average roughness of CrN thin films prepared on grounded and floating substrate using $U_- = -800$ V, $U_+ = 230$ V, $pw_- = 5$ µs, $pw_+ = 30$ µs and different magnetic field configurations.

3.2.3. Mechanical Properties of Thin Film

The influence of the magnetic balance degree on the mechanical properties of CrN films is presented in Figure 14.

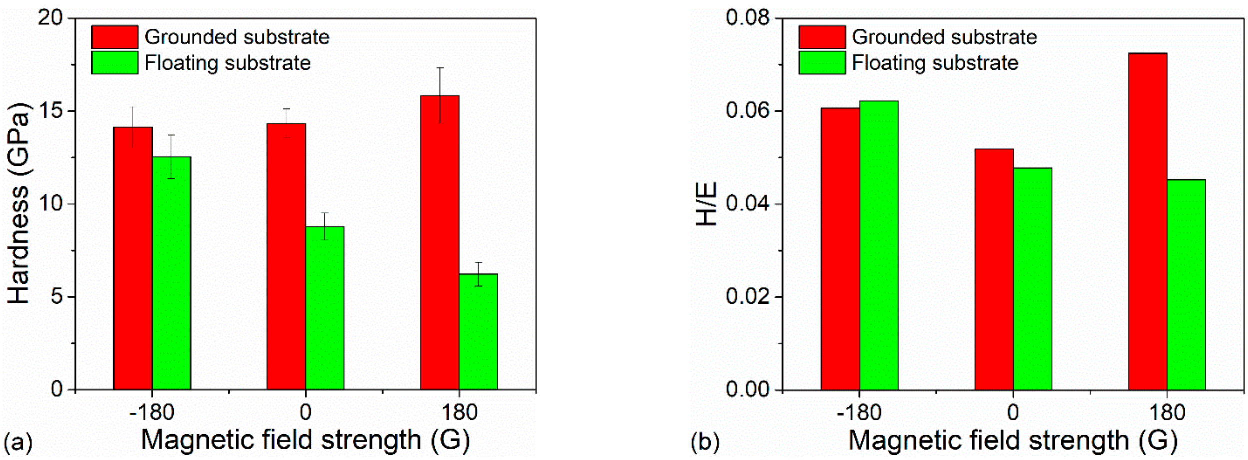

Figure 14. Hardness (**a**) and H/E ratio (**b**) of CrN thin films prepared by bipolar-HiPIMS on grounded and floating substrates using $U_- = -800$ V, $U+ = 230$ V, $pw_- = 5$ µs, $pw_+ = 30$ µs and different magnetic field configurations.

As the magnetic balance degree is changed from unbalanced type II to unbalanced type I magnetic configuration, the hardness and H/E ratio of the films deposited on floating substrates increase, reaching values close to those found for the films deposited onto grounded substrates. The results obtained for CrN films deposited on floating substrates show a significant relationship between the mechanical properties and the magnetic field configuration. The most significant difference in the mechanical properties occurs during the deposition with magnetically unbalanced type II configuration, where during the deposition onto floating substrates, the ion acceleration occurs only for a very short time, at the beginning of the reverse pulse. The change in the cross-sectional morphology of the films, from dense to an open porous structure, when changing the deposition conditions from grounded to floating substrate, results in an enormous decrease in the hardness. During the deposition with magnetically unbalanced type I configuration, the mechanical performances of the films deposited on floating substrates approach those of the films deposited onto grounded substrates, indicating a pronounced influence of the ion bombardment. This result is consistent with the results presented in Figure 10, which show that during bipolar-HiPIMS with an unbalanced magnetic degree type I, the plasma ions are accelerated during the entire positive pulse to energy corresponding roughly to more than a half of the reverse target potential. The absence of growth defects such as droplet defects and/or inter-columnar voids together with dense structures (as shown in Figure 12) also contributed to the enhancement in the mechanical performance. All these results emphasize the importance of choosing the proper pulsing and magnetic field configurations in order to gain maximum benefits of bipolar-HiPIMS deposition on floating substrates.

The coefficient of friction was estimated by dividing the friction force to the normal load applied on the indenter. For all CrN films, deposited using different pulsing and magnetic field configurations, the evolution of friction coefficient shows small fluctuations, without any evidence of material failure or delamination, with mean values ranging between 0.14 ± 0.02 and 0.17 ± 0.02. As it was expected, the lowest value of the coefficient of friction was obtained for the CrN film deposited on grounded substrate using unbalanced magnetron type II, which has higher hardness and lower roughness as compared to the other films. This result is in good agreement with other reported data which show that the coefficient of friction decreases with an increase in hardness and decrease in the surface roughness [13,19,23,42,43].

4. Conclusions

The structural and mechanical properties of CrN thin films deposited by bipolar-HiPIMS were tuned by a proper selection of pulsing and magnetic field configurations, which allows controlling the energy and flux of ion bombardment of the growing film. It was found that both ion energy (controlled through the reverse target voltage) and ion flux (controlled through the ion current density, via coil current) are playing a key role with respect to the films' microstructure and mechanical properties. The positive pulse duration and magnetic field variations are accompanied by clear changes in the crystallinity, morphology, microstructure, and mechanical behaviour of the films deposited on floating substrates. Simulating an unbalanced magnetron type II, it was found that there is a very short time of ion-acceleration immediately after applying the reverse pulse, while for an unbalanced magnetron type I, the acceleration voltage is close to the applied target voltage at the beginning of the reverse voltage, slowly decreasing during the reversed pulse. During the deposition on floating substrates, a clear ion bombardment effect was detected when short negative pulses, relative long positive pulses together with an unbalanced magnetron type I configuration were used. By increasing the positive pulse duration, the film's properties (microstructure and hardness) approach those of the films deposited onto grounded substrate. On the other hand, a much smaller effect was observed when long negative pulses, short positive pulses or an unbalanced magnetron type II configuration were used. Based on the presented results, we can conclude that the bipolar-HiPIMS discharge is extremely effective in preparing dense films onto floating substrates with excellent mechanical properties if the pulsing and magnetic field configuration are properly selected.

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