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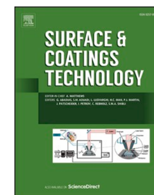

Pulse length selection in bipolar HiPIMS for high deposition rate of smooth, hard amorphous carbon films

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ABSTRACT

Amorphous carbon films were deposited by bipolar HiPIMS, as a function of negative and positive voltage pulse lengths (50-175 μs and 0-175 μs respectively), using argon as sputter gas. The deposition rate, compressive stress, sp^3 fraction and mechanical properties of the films were investigated and the results compared with those of amorphous carbon films deposited by conventional unipolar HiPIMS. We found minimum threshold positive and negative lengths are required in bipolar HiPIMS to enhance the sp^3 fraction above 45 % and reduce the argon content. In addition to increasing the flux and energy of depositing ions by electrostatic control, bipolar HiPIMS also increases the flux ratio of depositing ions to sputter ions and thus reduces the probability of sputter gas incorporation into the growing amorphous carbon layers. Reduced argon content in the coatings correlates with high residual stress, high hardness and evidently enhanced tool cutting functionality.

1. Introduction

Deposition rate remains a limitation on the application of high-performance wear-resistant amorphous carbon films deposited by the direct current magnetron sputtering process, owing to the low sputtering yield of graphite sputtering targets in conventional processes. Examples of methods that deliver high deposition rates for carbon films are filtered cathodic arc deposition [1], high frequency short pulse High-power impulse magnetron sputtering HiPIMS [2,3,4] and mixed mode HiPIMS [5–7]. These methods offer, in addition, an ionized deposition flux that, when used with appropriate substrate bias, imparts energy to the ions, bombarding the films during growth in the process known as ion-assisted deposition, to achieve desirable properties. These properties include high hardness and wear resistance, usually accompanied by a high content of sp^3 bonded carbon atoms. A potential disadvantage of these methods is the production of macroparticles from the target that become incorporated into the deposited layers.

HiPIMS is becoming one of the leading sputter coating methods for depositing a variety of metallic [8,9], ceramic [10,11], carbon and carbon-based coatings [12] with customized properties to meet specific industrial application needs. Increasing the deposition rate in HiPIMS remains a challenge, since it has been reported that the HiPIMS deposition rate is typically lower when compared to conventional DC magnetron sputter deposition operating at the same average power [13]. Ionized flux deposition is a key advantage of HiPIMS and the enhancement of coating quality in HiPIMS is strongly correlated with the ratio of the ion flux to the neutral atom flux transported into the substrate [14–20]. In HiPIMS for the deposition of carbon films specifically, the ionization rate of sputtered carbon species in the plasma is comparatively low, owing to the combination of a low sputtering yield of carbon

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[21], a high ionization energy and a low reaction rate due to the small collision cross section between the carbon atoms and electrons in the plasma [22].

In order to increase the ionization of sputtered carbon atoms, several techniques have been implemented. These include using neon as the sputter gas [23,24], operating HiPIMS in a mixed mode where a short-lived arc forms due to the sputter current runaway [3,5–7,24,25] and using stronger magnetic field configurations [7,26]. Utilizing an external magnetic field has been applied using a current-carrying coil to transport high numbers of depositing ions towards the substrate [27]. Although these techniques have achieved success in increasing the carbon ion to neutral ratio, the incorporation of background gas atoms in the amorphous carbon matrix of the film is a potential disadvantage. Also, the application of an external magnetic field by positioning the coil between the target and substrate to focus the ions may increase the relative flux of ions [7,15] but may limit the overall coating deposition rate, leading to a disadvantage for industrial coating processes.

Here we assess bipolar HiPIMS as a method of depositing carbon films under ion bombardment. In bipolar HiPIMS each negative pulse is followed by a positive pulse intended to drive positive ions away from the target towards the substrate. Keraudy et al. [28] studied the ion propagation dynamics in bipolar HiPIMS as a function of amplitude and duration of the positive pulse and provided evidence that a short negative pulse followed by a positive pulse of high amplitude accelerates ions, in this case titanium, to the substrate, increasing their energy of impact. These authors found a maximum in the ion energy distribution at the energy corresponding to the voltage of the positive pulse. Viloan et al. [29] studied bipolar HiPIMS, also using a titanium target, and reported that a relatively short negative pulse of about 20 μs is needed with a relatively long positive pulse to accelerate the most ions towards the substrate. Bipolar HiPIMS also promises a higher deposition rate than conventional HiPIMS [30]. However, the findings of previous work for metal deposition cannot be directly translated to carbon, since carbon is a low sputtering yield material, and short negative pulse lengths may not give a sufficiently high coating rate. It has been shown that for a carbon target, the use of bipolar HiPIMS increased ion generation and transport to the substrate and was associated with enhanced sp^3 fraction, up to approximately 50 % for a positive pulse voltage of 200 V [31]. However, the control of the sp^3 fraction of carbon and the upper limits to the fraction of tetrahedral bonding by adjusting the pulse length and voltage of both the positive and negative pulses and the incorporation of sputter gas atoms into the coatings by bipolar HiPIMS have not been fully explored. A significant challenge is to achieve sp^3 fractions in carbon films up to or exceeding 75 %, which is achievable by some ion-assisted methods [32].

In the current work, the effect of varying both the positive and negative voltage pulse length on the production, transportation, and deposition of carbon ions in bipolar HiPIMS is investigated. By controlling the negative and positive pulse lengths, the amount and energy of ion bombardment relative to the neutral deposition could potentially be controlled to optimize the structure and properties. In addition, the incorporation of the argon sputter gas into the coatings as a function of bipolar pulse parameters, and its correlation with sp^3 fraction, coating smoothness, compressive stress and tool cutting performance is studied. The results will be helpful in determining the operating parameters for the applications of carbon coatings.

2. Experimental methods

Substrates consisting of 1 cm × 1 cm n-type Si (100) wafer slices, were thoroughly cleaned ultrasonically followed by alkaline detergents and de-ionized water and isopropanol. The depositions were carried out in an AJA sputtering system pumped down to the base pressure of 10^{-7} Torr (1.33×10^{-7} Pa) using a turbomolecular pump as shown in Fig. 1. The coating system was equipped with circular magnetron sources described elsewhere [10,15,24] operated with compressed graphite (99.995 % carbon, Plansee Composite Materials GmbH in Lechbruck, Germany). The substrates were located at 11 cm from the target during the deposition process. Once the base pressure was achieved argon sputtering gas was admitted and the working pressure was set to 2.25×10^{-3} Torr (0.33 Pa). Few experiments have been performed at 4×10^{-3} Torr (0.53 Pa) to determine argon content at higher pressures. The target was connected to a 6-kW bipolar pulsed power supply (model 6 kW HiPIMS, hipV Spain) capable of operating up to the maximum power of 6 kW in regular HiPIMS mode either delivering only the negative voltage pulse or delivering a bipolar combination of a negative voltage pulse followed by a positive voltage pulse. The applied voltage was −450 V for the negative pulse, and +150 V for the positive pulse. The pulse length for the negative voltage was varied in the range of 50–175 μs, while for the positive pulse, the range was from 0 to 175 μs. The substrate is electrically connected to the bias power supply delivering −60 V invariably through the strong capacitor (900 μF) attached to it. Operating at the frequency of 250 Hz, the processes were carried out by various negative pulse lengths in the range from 50 to 175 μs. The power increases over the range from 0.25 to 0.8 kW. The dissipated power is calculated from the area under the curve corresponding to the negative

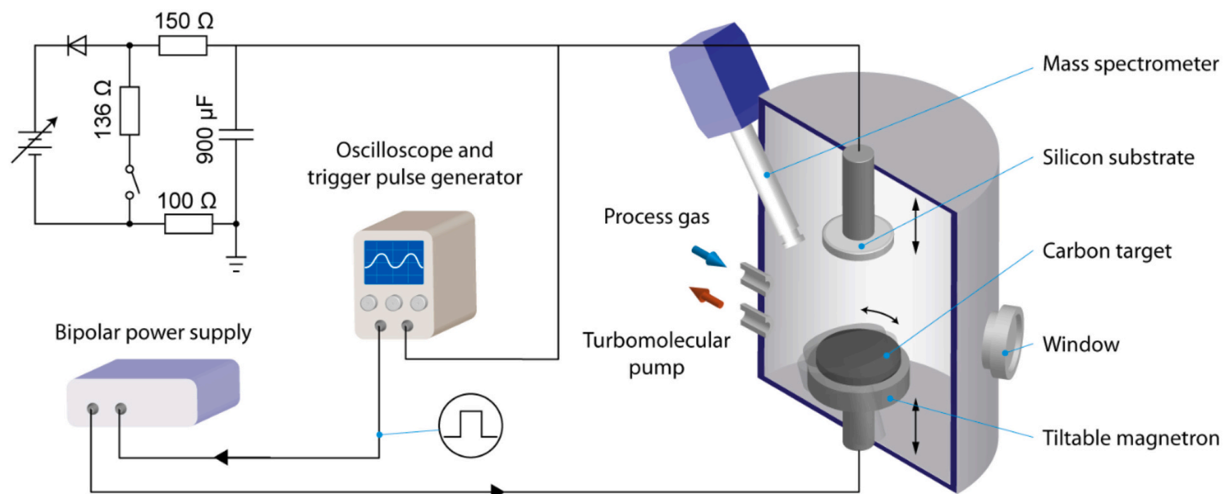

Fig. 1. A schematic figure of the coating system equipped with a bipolar HiPIMS power supply, connected as shown. A mass and energy selective quadrupole spectrometer are attached to the system to study the flux of argon and carbon ions generated and transported to the coating substrate. The magnetron target can be tilted either towards the substrate or towards the mass spectrometer.

voltage and current pulses only. More than 60 samples were deposited at various bipolar voltage pulse lengths; coating properties were investigated for stress, hardness, elasticity, carbon (sp^3) content, argon content and roughness.

An energy-resolved mass spectrometer (PSM 003, Hiden Analytics limited, UK) was used to analyze the energy distribution of the ions and neutral atoms of argon and carbon. The system has a Quadrupole mass filter, an electron multiplier and is connected to an energy analyzer for ion detection and analysis. The analyzer part of the mass spectrometer is maintained at a base pressure of $<10^{-8}$ Torr (1.33×10^{-6} Pa) using a differential pumping system equipped with a turbomolecular pump and a membrane pump. Excellent signal-to-noise ratio was maintained by setting the dwell time to 0.2 s. The instrument was mounted in front of the magnetron racetrack at a distance of 11 cm by tilting the magnetron cathode away from the substrate holder and directing it towards the opening of the mass spectrometer.

The thicknesses of the coatings were measured by stylus profilometer with a 0.5 nm vertical resolution (Alpha-Step D-500 stylus, KLA technologies). Accurate roughness values are obtained by using cut-off heights by appropriate software filters to distinguish between the components belonging to roughness and waviness. Macroparticle analysis is also included by measuring the samples using the profiler scanned over an area of 1×1 mm^2. Valleys in the scanned surface profile with a size larger than 50 nm are considered as a macroparticle in the carbon layers. More than 10 measurements have been taken for each sample and the mean is presented with error bars. Argon content of the deposited coatings were determined by Rutherford backscattering spectrometry (RBS) using 2 MeV He^+ ion. The spectral results obtained were analysed by RUMP simulation software. Hardness and elastic modulus were measured by nanoindentation measurements using a Hysitron TI 950 nanoindenter. High accuracy in the reported values of hardness and elastic modulus was maintained by averaging the values for each sample (of ≈150 nm thick) over 20 indentation measurements during loading and unloading using the maximum load of 10mN. The residual stress of the coatings was estimated using Stoney's method [33] that uses the difference in the radius of the substrate curvature before and after coating. Using a stylus profilometer (Alpha-Step D-500 stylus, KLA technologies), the radii of curvature were measured in orthogonal directions along the x and y axes of the samples that are square in size. Five measurements were taken on each direction. The average values measured for each direction before and after deposition of coatings were used to calculate stress using Stoney's method.

The sp^3 content of the carbon in the coated samples was evaluated from the C1s spectra obtained by performing Al Kα source (1486.7 eV) X-ray photoelectron spectroscopy (XPS) (SPECS XPS model XR 50) on the samples. The background contribution was removed using the Shirley method. Different carbon components sp^3, sp^2 and carbonyl groups of C1s peaks were fitted using CASA XPS software with a combination of Gaussian and Lorentzian functions with partial contributions of 70 % and 30 % respectively. The range of values for the peak positions and peak widths (FWHM) for the different carbon components were set to the values described elsewhere [3] and were allowed to vary within the prescribed limits during the fitting procedure to achieve the best fit. Wet Machining tests were performed by a vertical milling machine using tungsten carbide-cobalt inserts (Swiss tools) on the annealed maraging steel (MDN250). As the translation of coating properties from Si wafers to tool substrate is different, Cr interlayer has been used to keep the adhesion to HF1 level. However, no changes in the any of the amorphous carbon (aC) film properties owing to the change in substrate and to the introduction of the Cr interlayer are expected as the mechanical property of aC is purely depending on the depositing ion impact with optimized energy.

3. Results

Fig. 2 shows the current to the target and the current to the substrate

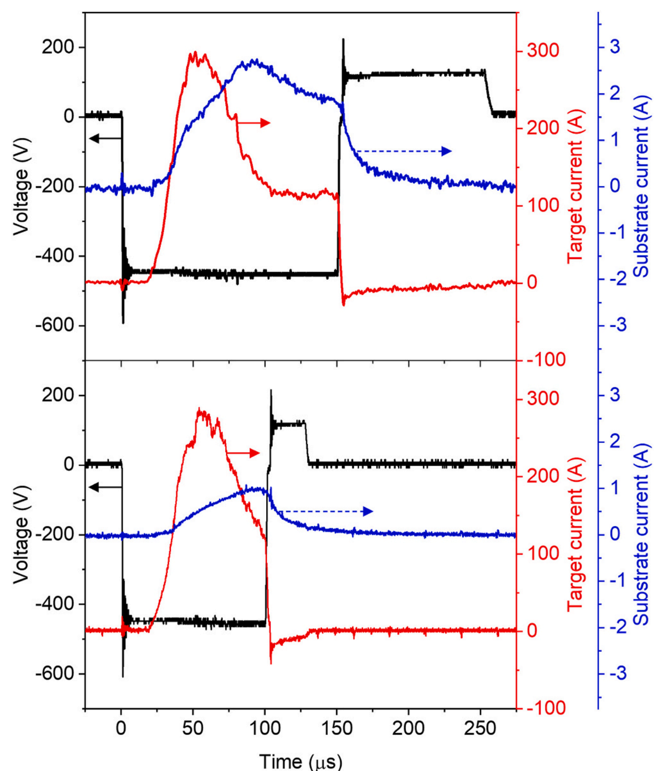

Fig. 2. The target voltage (left axis, black line) begins with a negative pulse followed immediately by a positive pulse, $\tau_{npl}$is the negative pulse length and τ_{ppl} is the positive pulse length. The discharge current is represented in the red line on the right axis. The top panel shows $\tau_{npl}$of 150 µs and a $\tau_{ppl}$of 125 µs and the bottom panel is for τ_{npl} of 100 µ s and a $\tau_{ppl}$of 25 µs. The net substrate current indicated by the dashed arrow (extended axis; blue line) represents the ion current collected at the substrate (biased at −60 V) while the net discharge current (right axis, red line) changes polarity when the polarity of the voltage pulse reverses. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

as a function of time from the onset of each bipolar voltage pulse set applied to the target, consisting of a negative pulse and a positive pulse with no delay between them. The substrate current is an ion current during both polarities of the pulse, while the target current is an ion current during the negative pulse and a small electron current during the positive pulse. The larger part of the power dissipation occurs during the negative pulse, with a relatively small contribution from the positive pulse. For a typical case of a negative pulse length as in Fig. 2a of 150 µs and a positive pulse length of 125 µs, the energy dissipation during the positive pulse only makes up 2.2 % of the total power dissipation. The behaviors of the currents are explained by a mechanism in which ions are drawn to the substrate by the substrate bias during the negative target pulses and during the positive target pulses ions are driven away from the target and also impact the substrate as proposed by Huber et al. [34] and further described by Fernández-Martínez et al. [35].

Fig. 3 shows that the deposition rate of carbon in the bipolar HiPIMS process is increased substantially for a given negative pulse length, by adding a positive pulse. By optimum selection of negative and positive pulse lengths, a maximum deposition rate of almost 3 nm/min is achieved. The same combination of long negative pulses and long positive pulses gives the most charge collected at the substrate (Fig. 4), as assessed by measuring the charge carried by ions with energies <40 eV. Most of the positive charge is collected during the negative portion of the target pulses, but this amount of charge is increased with the length of the positive pulses applied to the target (Fig. 4b).

Fig. 5 shows the argon content of the film as a function of positive pulse length, negative pulse length and pressure. The maximum argon

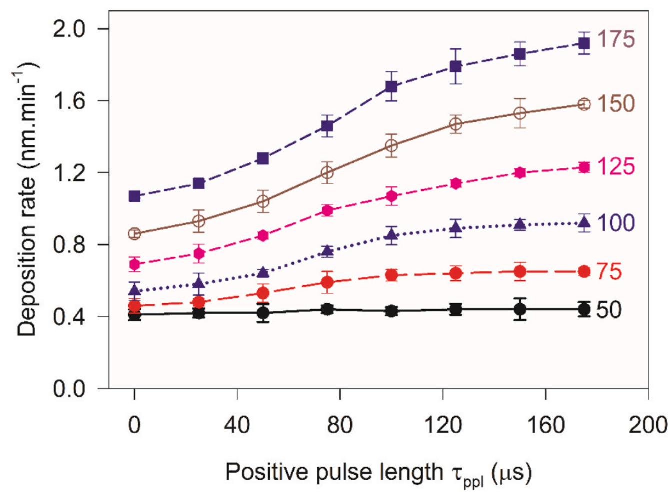

Fig. 3. The deposition rate on the substrate as a function of the positive pulse length for positive pulses applied immediately after each negative pulses at a pulse repetition frequency of 250 Hz. The numbers labeled on the curves show the duration (in microseconds) of the corresponding negative pulses. Note that the deposition rate is increased by increasing the length of both the positive and negative pulses.

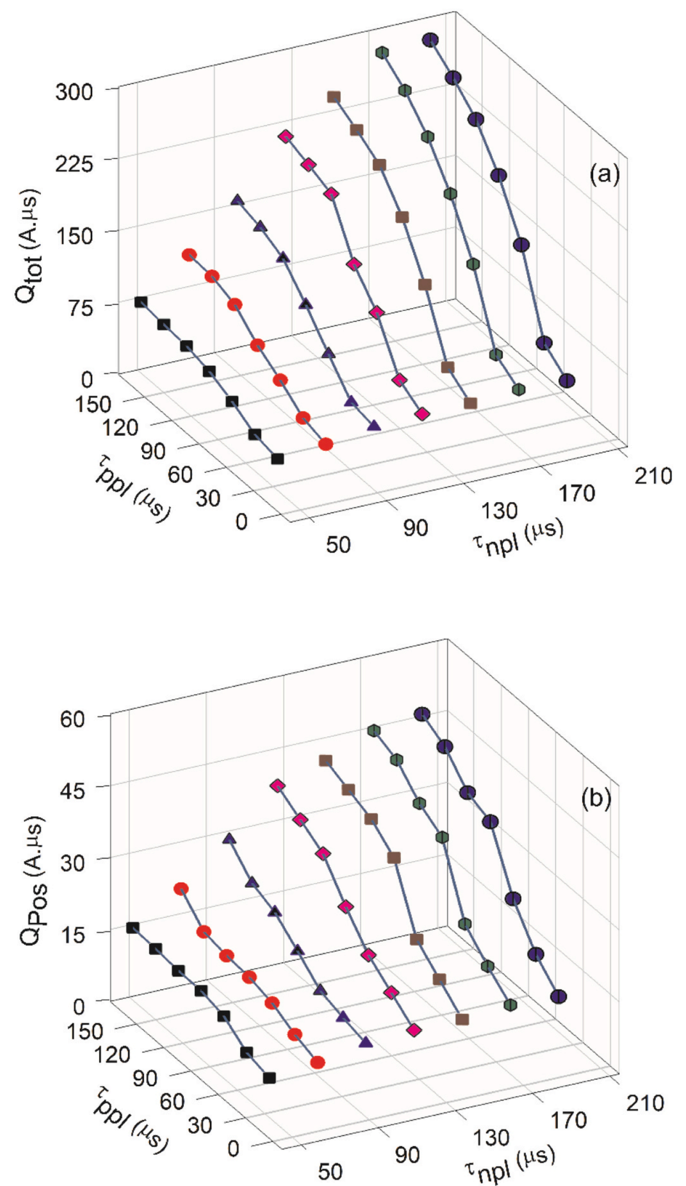

Fig. 4. a. The net positive charge (predominantly ions), collected at the substrate during one complete bipolar cycle as a function of both the positive and the negative pulse lengths. The colour scale, in µC, indicates the net positive charge collected. Maximum charge is collected when both positive pulse lengths (τ_{ppl}) and negative pulse lengths (τ_{npl}) are maximum. Panel b. The positive charge (predominantly ions) collected at the substrate during the application of the positive portion only of one complete bipolar pulse cycle.

content occurs for short positive pulses and higher pressures. Fig. 6 shows the compressive stress of the carbon films as a function of negative and positive pulse lengths. Maximum compressive stress is generated in coatings that have less argon content.

Fig. 7 shows the hardness, modulus, and roughness of the films as a function of negative and positive pulse lengths. All properties are optimized by the combination of long negative and long positive pulses. The H/E ratio, also shown in Fig. 7 is increased by increasing the positive pulses lengths. Compressive stress also increases with longer pulse length for a given negative pulse length (Fig. 6).

Fig. 8 shows the macroparticle contents (valley of size >50 nm) in the amorphous carbon films as a function of negative pulse lengths τ_{npl} (ranging from 100 to 175 µs) for three different positive bipolar voltage pulse lengths τ_{ppl}. The trendline clearly demonstrates that the increase in the length of the negative voltage pulse τ_{npl} increases the amount of macroparticles, while the longer positive pulse lengths τ_{ppl} reduce the amount of macroparticles. Application of positive pulses helps to reduces the roughness of the deposited films (c.f Fig. 7d).

Fig. 9 shows the XPS results of an evaluation of the sp^3 content in the carbon coating, together with an example of the C1s XPS spectrum used for the analysis. A maximum sp^3 content occurs for coatings with long negative and long positive pulse lengths. The sp^3 content reaches a plateau in its dependence on positive pulse length when combined with the longest negative pulse lengths. This correlates with Fig. 10 that represents the mass spectrometer measurements of increasing ion to neutral ratio for carbon and argon species in the plasma. There is also a plateau in the sp^3 content as a function of negative pulse length for the longest positive pulse length. Together these results cover all combinations of negative and positive pulse lengths and show that the maximum sp^3 content has been reached in our bipolar HiPIMS process. While the negative HiPIMS voltage pulse should be long enough to generate a sizeable amount of carbon ions close to the target region, the duration of the positive pulse ought to be sufficient to accelerate significant fraction of those carbon ions away from the target towards the substrate.

Fig. 10(a–d) show the different effects of increasing the negative and positive pulse lengths. Using the energy selective filter, the mass spectrometer was configured to exclusively measure ions with energies greater than or equal to 40 eV in order to calculate the energetic ion content ratio of carbon to argon (Fig. 10d).

Fig. 11 represents the measured flank wear as a function of machining time estimated from the machining test performed on the annealed maraging steel. Machining tests are carried out using the tungsten carbide-cobalt inserts coated with amorphous carbon at different positive pulse lengths for the 150 µs negative HiPIMS pulse lengths. An optimum combination of positive and negative pulse lengths (both at 150 µs) exhibited better performance with minimal flank wear.

The results reveal that for a given machining time, the flank wear is reduced by almost 50 %, thus significantly increasing the lifetime of the tool by almost twofold. The improved surface finish (reduction in macroparticles and lower roughness), higher sp^3 content, compressive stress, hardness, Young's modulus, and H/E ratio of the optimized coatings as characterized in this work are believed to all contribute to this significant improvement in coating functionality.

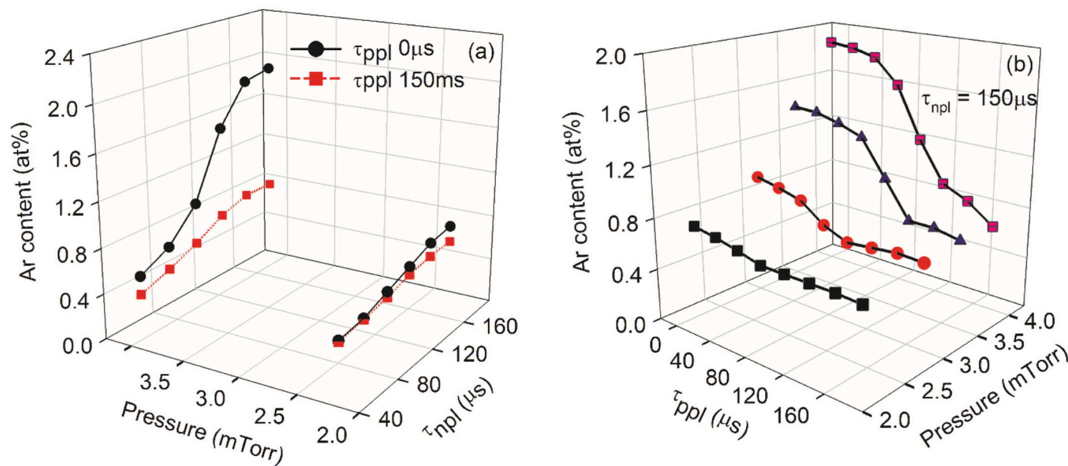

Fig. 5. a The argon content of the film measured using RBS in at.% as a function of the negative pulse length (τ_{npl}), at two different pressures, positive pulse lengths (τ_{ppl}) of zero and 150 μs. The maximum argon content occurs for long negative and short positive pulses at higher pressures. b The argon content of the film measured using RBS in at.% as a function of the positive pulse length, at four different pressures for the negative pulse length of 150 μs. The maximum argon content occurs for short positive pulses and higher pressures.

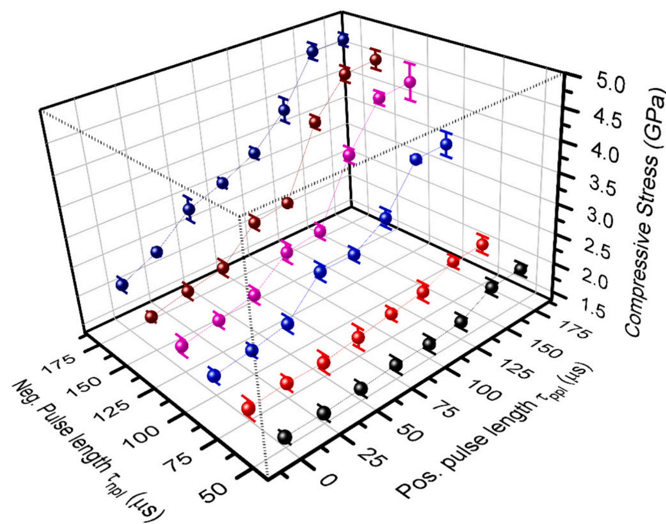

Fig. 6. The compressive stress in the coatings increases with positive pulse length and also with negative pulse length, correlating with the sp^3 content as shown in Fig. 9. There is a saturation in compressive stress for long positive pulses at the maximum negative pulse lengths.

4. Discussion

This work has results of importance in both the science and the applications of the bipolar HiPIMS deposition mode. Important scientific findings are the new evidence for the mechanism behind the increase in deposition rate when the bipolar mode is used and an understanding of the limits to the sp^3 content. As in conventional HiPIMS, the negative pulse attracts positive carbon ions and gas ions to the target, causing sputtering of carbon atoms. The sputtered carbon atoms are ionized by the dense HiPIMS plasma. Meanwhile any remaining positive charge on the substrate is neutralized by electrons. The bipolar mode then applies a positive pulse which allows the carbon ions to be efficiently transported to the substrate by electrostatic repulsion from the target region.

There is an increased level of carbon ion bombardment of the coatings during growth on the substrate, attributed to the efficient transport of carbon ions to the substrate. This increased level of ion bombardment of the coatings occurs when long negative pulses are combined with long positive pulses and is higher than for conventional HiPIMS. The increase in ion bombardment leads to increases in the sp^3 fraction and the compressive stress level, a good outcome for the high-rate deposition of coatings with a moderately high sp^3 fraction, although the sp^3 content is not as high as generally observed for mixed mode HiPIMS where 72 % sp^3 content is achieved [5,6,36]. The reason for the lower sp^3 content may lie in the energy distribution of the ions. Although the chosen positive pulse voltage (+150 V) aligns with the expected optimum energy for creating tetrahedral bonding in amorphous carbon films, the energy distributions found by Keraudy et al. [22] show a maximum energy at the value of the positive voltage pulse (150 eV in our case), there is a long tail of higher energy ions. Even though the results of Fig. 10 a show that the total number of carbon ions relative to argon ions is still increasing with negative pulse length for long positive pulses, and the number of energetic carbon ions is still increasing with positive pulse length for long negative pulses, the saturation in sp^3 content shows that these carbon ions are becoming less effective at creating sp^3 bonds. The reason may be that the carbon ions may have reached the point where they cause a stress relief in our carbon deposition process, limiting the level of compressive stress to the value we see (a maximum of 4.7 GPa for the longest positive and negative pulses). This value is consistent with the results shown in Fig. 7 of reference [32] which shows that a compressive stress level of 4.7GPa is at the edge of the range required to generate significant sp^3 bonding and a compressive stress above 6GPa is required to generate sp^3 fractions above 75 %. Earlier work [37] using experiment and simulation showed that there is an energy window effect for compressive stress generation by ion impacts and if the energy is too high, stress relief occurs.

The argon content in the films is minimized using the positive pulses in the bipolar mode, so that there is a double benefit of high sp^3 content and low argon content. These findings are consistent with carbon ion rather than argon ion bombardment being the cause of the highest levels of compressive stress and sp^3 fraction in this sputter deposition process. The active transport of carbon ions produced near the target towards the substrate during the positive pulses of the bipolar HiPIMS is clearly beneficial to the coatings.

The lowest macroparticle content is achieved in bipolar mode for long positive pulses. The rapid termination of incipient arcs at the end of each negative pulse by means of the positive pulse, is the likely reason, reducing the opportunity for cathodic arc spot formation which could lead to macroparticle generation. A further benefit of longer negative pulses is that the sputtered carbon ions dominate in the plasma over argon ions which are dominant at shorter negative pulse lengths, reducing the argon content in the films and increasing the sp^3 creation

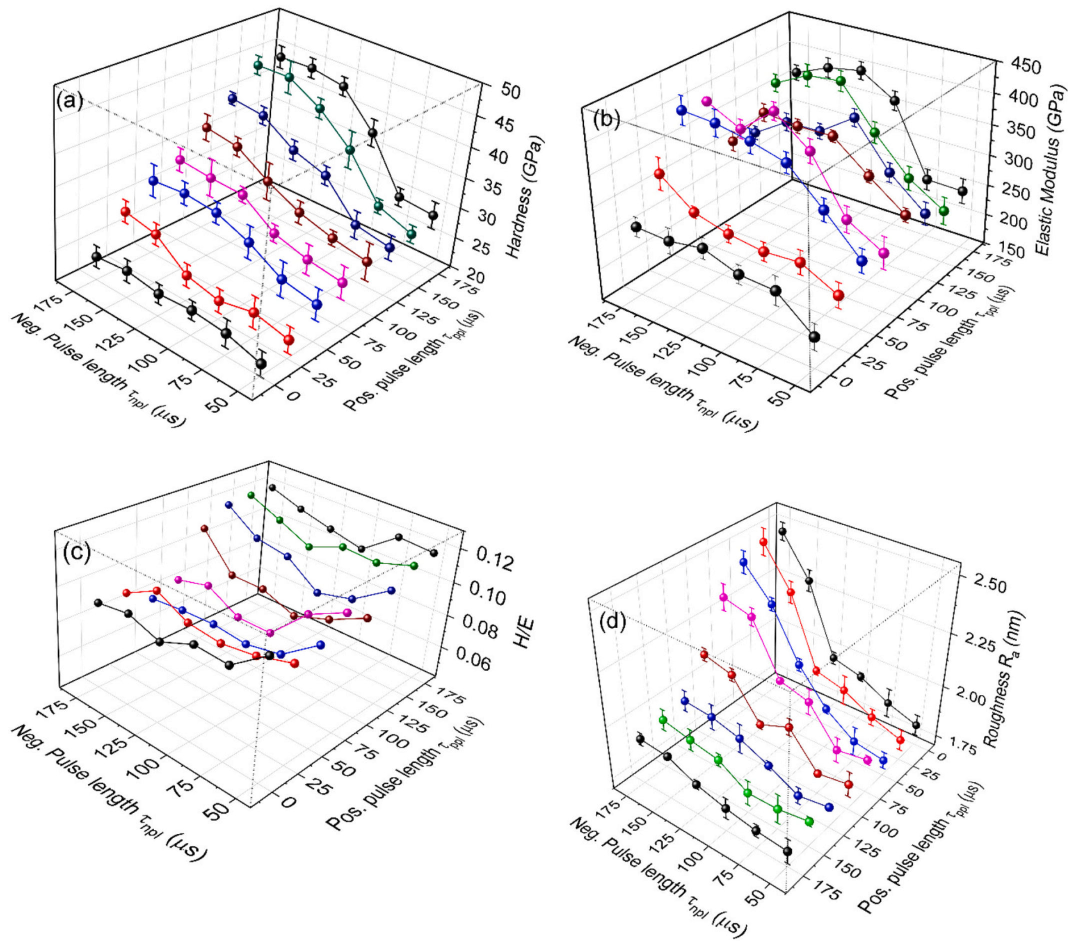

Fig. 7. a The hardness values for the coatings deposited as a function of negative and positive pulse lengths. The hardness values saturated for 150 μs of negative pulse length and 150 μs of positive pulse length. The hardness values reach a plateau for the longest positive and negative pulses. The saturation may be caused by the limit on the number of sputtered ions available. b The elastic modulus increases with increasing positive pulse length. c The hardness to elastic modulus ratio H/E increases with increasing positive pulse length. d The RMS roughness as a function of positive and a negative pulse length. The roughness increases with negative pulse length and decreases with positive pulse length.

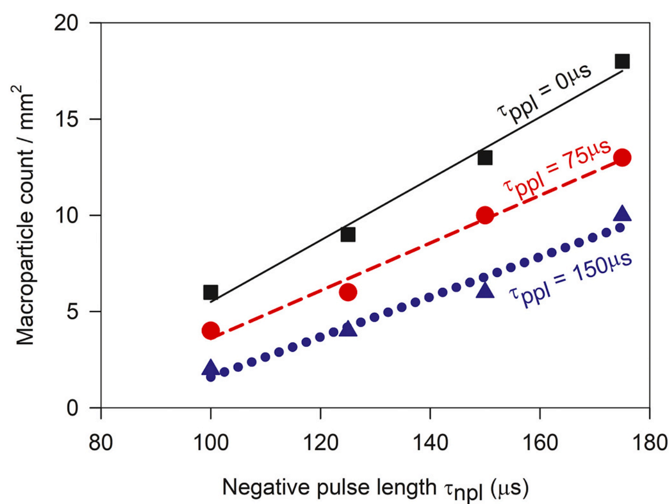

Fig. 8. The number of macroparticles per mm^2 as a function of negative pulse length for three different positive bipolar voltage pulse lengths (marked along the trendline). Application of positive pulses evidently reduces the chance of macroparticle formation.

by carbon ion bombardment. A longer positive pulse allows for deposition of all of the available carbon ions created in the preceding negative pulse. The main negative HiPIMS voltage pulse must have a minium threshold length in order to generate a significant quantity of carbon ions before the positive voltage pulse accelerates them. The length of the positive pulse should be long enough to accelerate the carbon ions near the target area as well.

The increase in deposition rate achieved by bipolar HiPIMS when using the combination of long positive pulses with long negative pulses is advantageous for the cost-effective deposition of high-performance carbon coatings. The addition of a long positive pulse allows up to a doubling of the deposition rate for long negative pulses (see Fig. 3) with only a minor increase in the average power dissipation (estimated to be <2.2 %, from the results in Fig. 2). This finding may enable bipolar HiPIMS to become competitive with conventional DC magnetron sputtering deposition in terms of deposition rate at the same average power, since a doubling of deposition rate without significant additional power dissipation would place bipolar HiPIMS in the range 60 %–170 % of the DC magnetron sputtering rate at the same average power. The ability to form coatings with high sp^3 fraction at high deposition rate is important for tool coatings intended to be used for large volume production.

Coatings with high sp^3 fraction have low roughness that extends the life of titanium nitride tools when added as a topcoat on titanium nitride [38]. The availability of a sputtering technique like Bipolar HiPIMS that is capable of depositing high sp^3 fraction coatings is a significant development as sputtering alone can now be used to produce high

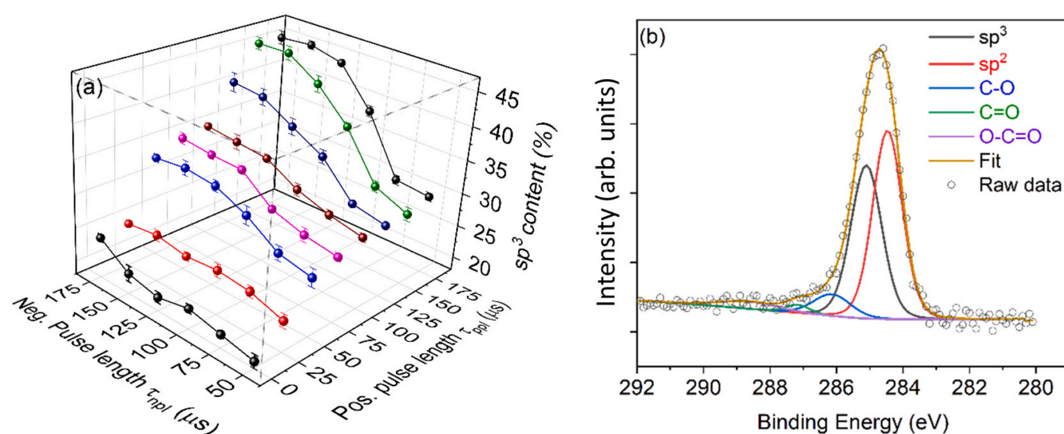

Fig. 9. a Pulse length dependence of the highest sp^3 content (sp^3 / (sp^2 + sp^3) × 100). The highest sp^3 content of 45.4 % occurs when the longest positive pulses are combined with negative pulses longer than 150 μs. b) shows an example of C1s XPS spectrum obtained from the amorphous carbon sample deposited at both negative and positive pulse lengths of 150 μs used to calculate the sp^3 content by deconvoluting the components shown.

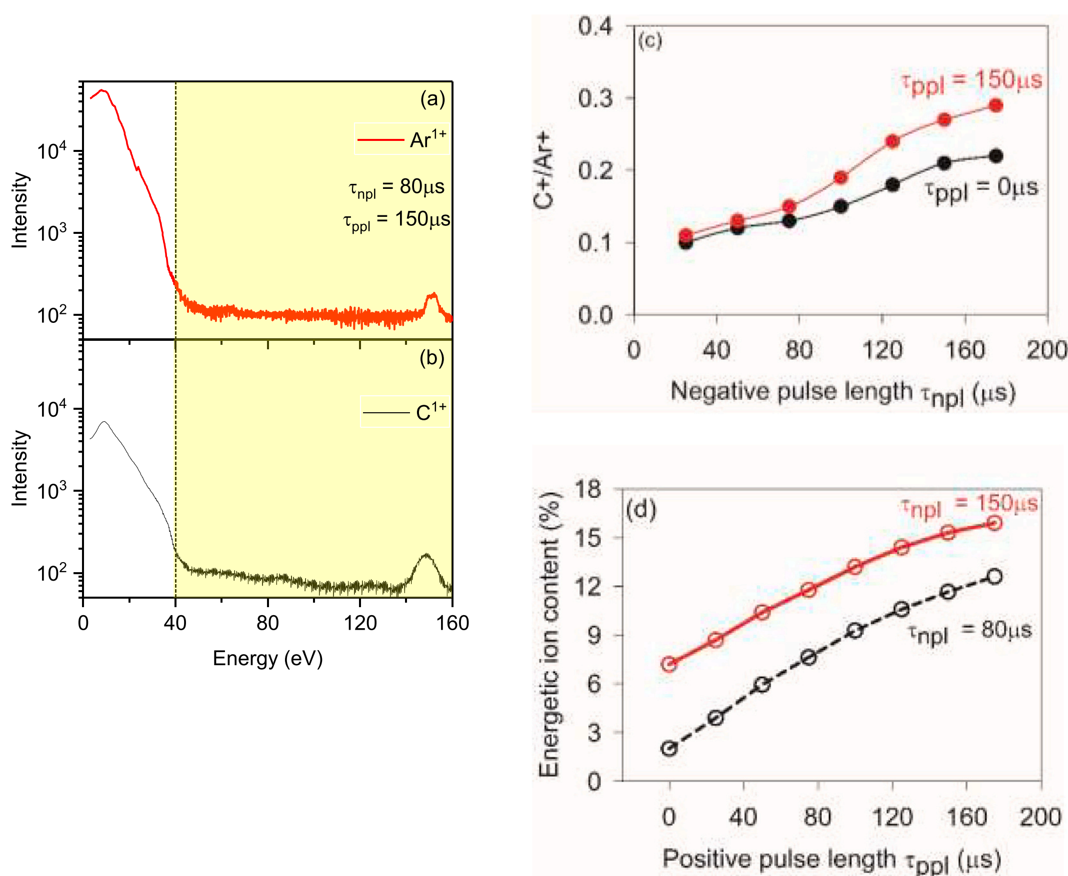

Fig. 10. Energy selective mass spectrometer measurements showing (a) the energy resolved spectrum of singly ionized argon ions and (b) singly ionized carbon ions for the negative pulse length of 80 μs and the positive pulse length of 150 μs. The shaded area of (a) and (b) represents the energy of the ions >40 eV (boundary marked with vertical dash lines). (c) represents the ratio of the total area under the spectral curve calculated for carbon ions to argon ions and (d) represents the sum of percent of energetic ions (>40 eV) of argon and carbon (shaded area) to all ions as a function of positive pulse length when bipolar pulses are applied with negative pulse lengths of 80 μs (black dashed curve) and 150 μs (red solid curve). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

performance low wear tool coatings in a single step process with a base layer (either Cr or TiN) and a carbon topcoat, which is demonstrated by the extended tool life by reducing flank-wear (c.f. Fig. 11).

5. Conclusions

In this paper, we have shown that the bipolar HiPIMS method, while increasing the deposition rate of carbon films also increases the sp^3 fraction of the films to a value of 45.4 % that is consistent with the degree of compressive stress we observe, but so far does not reach the

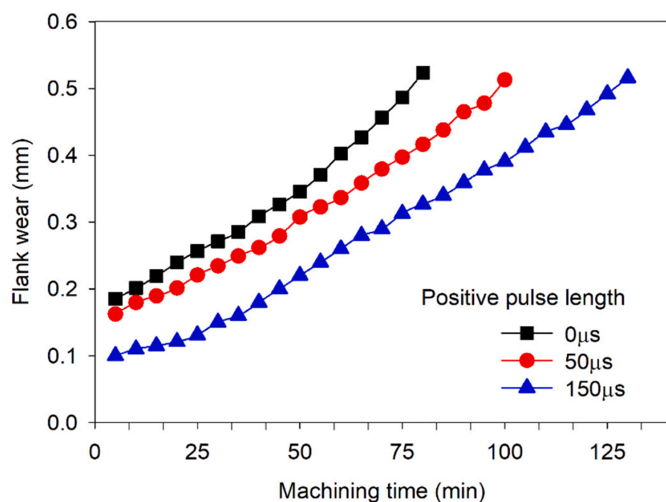

Fig. 11. Flank wear as a function of machining time is presented for amorphous carbon coatings deposited on a cutting tool at different positive pulse lengths for 150 μs negative HiPIMS pulse lengths. Flank wear was measured as a function of machining time at a spindle speed of 300 rpm; depth of cut is 0.4 mm at the feed rate of 50 mm/min. The combination of positive and the negative pulse lengths (both at 150 μs) exhibited the best performance with the least flank wear.

higher values of over 70 % that have been reported using other ion-assisted deposition methods. Further studies are recommended in which the positive voltage is reduced with the aim of minimizing stress relief by higher energy ions to increase the level of compressive stress in the coatings. We tested and confirmed the hypothesis that bipolar HiPIMS reduces the argon content of the films. Our findings support the proposition that the high deposition rate arises from driving positive carbon ions from the region of the target towards the workpiece, immediately after the ions have been created. Such a method retains the benefit of ionized deposition as in conventional HiPIMS but may be able to prevent the formation of an arc on the substrate surface and its subsequent progression to a crater that emits macroparticles at the final stage of the negative pulse. We have found that there is an optimum combination of positive and negative pulse lengths (both at 150 μs) that gives films with the highest deposition rate, highest sp^3 fraction and lowest argon content. Under these conditions the bipolar HiPIMS is estimated to have a deposition rate competitive with conventional DC magnetron sputtering for the same power dissipation. The smoothest films were obtained at the longest positive pulse lengths, for shorter negative pulse lengths, although the films remained relatively smooth at the longest pulse lengths when the negative pulse length was increased. The optimum time where the negative pulse should be terminated is after the arc forms, but before a crater that could emit macroparticles is established. The optimum time when the positive pulse should be terminated is likely to be the time when all positive ions have been driven towards the substrate. The cutting performance of the deposited films has been quantified and shows that the increased hardness, H/E ratio and higher sp^3 content established through the optimized negative and positive pulse lengths found in this work, contribute to a 50 % reduction in flank wear for a given machining time compared to films deposited without a positive pulse.

CRediT authorship contribution statement

R. Ganesan: Conceptualization, Methodology, Investigation, Visualization, Writing – original draft. **I. Fernandez-Martinez:** Conceptualization, Investigation, Visualization. **B. Akhavan:** Conceptualization, Methodology, Investigation, Visualization, Writing – review & editing, Supervision. **D.T.A. Matthews:** Investigation, Visualization, Writing – review & editing, Supervision. **D. Sergachev:** Visualization. **M. Stueber:** Conceptualization, Writing – review & editing. **D.R. McKenzie:** Conceptualization, Methodology, Investigation, Visualization, Writing – review & editing, Supervision. **M.M.M. Bilek:** Conceptualization, Methodology, Investigation, Visualization, Writing – review & editing, Supervision.

Declaration of competing interest

The authors acknowledge the financial support of the Australian Research Council (ARC) for this work. Furthermore, 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.

Data availability

Data will be made available on request.

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