

# Pulsed magnetron sputtering – process overview and applications\*

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The introduction of pulsed magnetron sputtering in the mid-90s initiated a new and exciting era in surface engineering technologies, which continues to develop. Pulsed sputtering transformed the deposition of 'difficult' materials, particularly dielectrics such as alumina, titania and silica. When sputtering in the mid-frequency range (20-350 kHz), the periodic target voltage reversals suppress arc formation at the target (a major problem during the deposition of dielectrics) and provide long-term process stability. Thus, high quality, defect-free coatings of these materials can now be deposited at competitive rates. However, pulsing the magnetron discharge in this frequency range also strongly modifies the deposition plasma; raising the time averaged electron temperature and the energy flux delivered to the substrate, in comparison with continuous DC processing. These advantageous deposition conditions have been exploited in the deposition of materials such as titanium nitride, where arcing is not considered a problem. In this case, coatings deposited by pulsed processing demonstrated enhanced structures and tribological properties in comparison with conventional coatings. This paper gives an overview of the pulsed magnetron sputtering process (pulsed DC and mid-frequency AC), describes the underlying plasma physics, gives examples of successful applications of this technology and briefly considers recent developments in this field, such as high power impulse pulsed magnetron sputtering (HIPIMS).

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## 1. Introduction

Continuous, i.e. DC or DC reactive, magnetron sputtering is a very successful technique [1]. In fact, in terms of the number of applications, it could be argued that this is the most successful of all the PVD techniques. Applications include tool coatings [2,3], corrosion-resistant coatings [4,5], data storage media [6], reflective coatings on mirrors [7], automotive [8], etc. However, all of these applications rely on either metallic coatings, or coatings such as metal nitrides that can be readily deposited by DC processes. The deposition of dielectric materials, though, is a very different proposition [9]. During the reactive deposition process, regions on the target adjacent to the racetrack become coated up, or 'poisoned' with an insulating layer of the reactive product (e.g. Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub>, etc.). The poisoned regions charge up until breakdown occurs in the form of an arc [10,11]. Arc events cause severe problems during deposition. Each event disrupts the reactive process control system and can lead to the ejection of a droplet of target material, which may cause a defect in the growing film. Furthermore, the power supply will momentarily shut down to attempt to quench the arc, thereby reducing the deposition rate. Thus arcs are detrimental to the structure, properties and composition of the coating and can lead to damage to the power supply.

## 2. The pulsed magnetron sputtering process

The problems associated with DC reactive sputtering of dielectric materials were largely overcome through the introduction of the pulsed magnetron sputtering (PMS) process in the early 1990s [12-15]. During pulsed sputtering, the target potential is periodically switched either to ground (unipolar mode) or to a positive potential (bipolar mode), at frequencies in the range 20-350 kHz. The most common mode of operation is the asymmetric bipolar one where, during the 'pulse-off' phase, the voltage is reversed to a magnitude equivalent to approximately 10% of the average voltage during the 'pulse-on' phase. Typical current and voltage waveforms at the target for the asymmetric bipolar mode are shown in fig. 1. Unlike radio frequency processes, in this frequency range both ions and electrons can follow the cyclic potential changes at the target and in the plasma. Thus, during the pulse-on phase an ion current is drawn at the target and the target is sputtered in the normal manner, but the poisoned regions on it may also charge up during this time. During the pulse-off phase, an electron current is drawn to the target, which can discharge the poisoned regions before breakdown, and arcing can occur [10,16]. One other point to note about the voltage waveform is the presence of a positive voltage overshoot at the beginning of the off phase.

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The magnitude of this overshoot can reach several hundred Volts [17] and, despite its short duration (<250ns), this feature has a significant impact on the discharge and, therefore, on the deposition process, as will be described later.

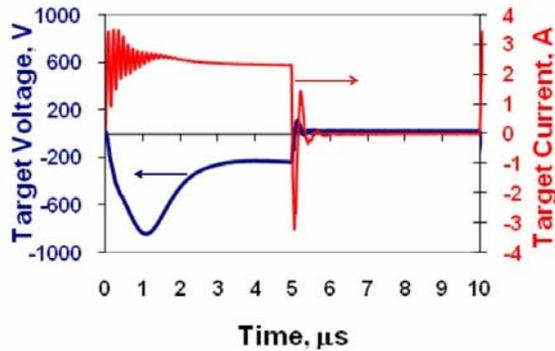


Fig. 1. Current and voltage waveforms taken from the Advanced Energy Pinnacle Plus power supply operating in pulsed DC mode at 100kHz pulse frequency, 50% duty.

If the poisoned regions are discharged completely, then arcs can be very effectively suppressed. However, if inappropriate operating conditions are chosen, then arcs may still occur, even during pulsed processing. The parameters effecting the arc rates have been studied in some detail, and it has been found that duty is one of the most significant factors, i.e., the relative proportion that the pulse-on period constitutes, compared to the full pulse cycle [18,19]. This is illustrated in fig. 2, which shows the cumulative number of hard arcs detected by the power supply (Advanced Energy MDX with a SPARC-LE V pulse unit) during the deposition of alumina coatings at a fixed frequency of 60kHz, but varying duties. As can be seen, at all of the duties tested, there was at least a short period of arc-free operation, but that once arcs begin to occur, the rate at which they occur increases exponentially. As the duty is decreased, i.e., the pulse-off time is increased relative to the on-time, the period of arc-free operation increases, until at a duty of 64%, over two hours of arc-free operation were achieved in this particular configuration.

One other problem encountered during the reactive sputtering of dielectric materials is the progressive loss of anode surfaces as the chamber walls become coated up. This phenomenon, referred to as the 'disappearing anode' [20,21], results in plasma parameters and, therefore, deposition parameters drifting with time, which is clearly undesirable. The loss of the anode surface has been simulated by the authors, by installing false walls inside a chamber [22]. The resistance to ground through these walls could be varied and planar probes were installed in the walls to characterise the discharge. The variation in the electron temperature and plasma potential with resistance to ground is shown in fig. 3. As the resistance increases, the plasma potential becomes progressively more negative

and the electron temperature increases. Thus, it is clear that it is becoming increasingly difficult to maintain the flow of current around the circuit formed by the power supply, chamber and plasma as the anode surfaces are effectively lost.

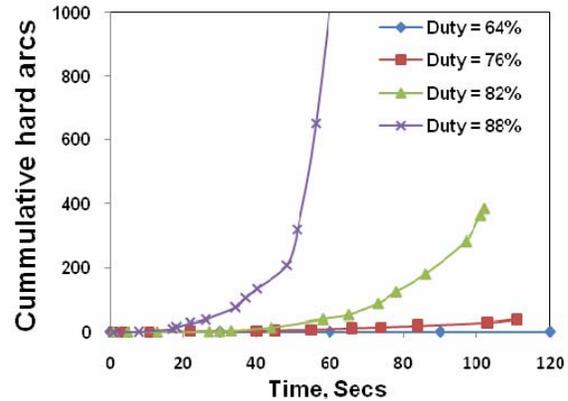


Fig. 2. The influence of the duty factor on the incidence of hard arc events during reactive pulsed magnetron sputtering of alumina films [18].

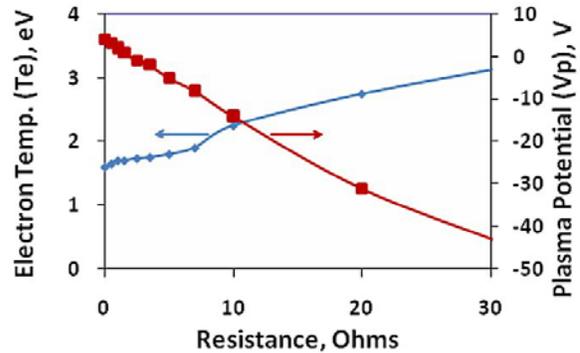


Fig. 3. Variation in the electron temperature and plasma potential with resistance to ground [22].

In addition to the disappearing anode problem, it is difficult to coat complex three-dimensional substrates from a single source. Thus, in industrial systems, magnetrons are generally arranged in pairs and operated in what is known as the dual bipolar mode [23,24]. In this mode, the magnetrons are driven at the same pulse frequency and duty (always 50%), but the pulse cycles are 180° out of phase. Thus, when one magnetron is 'on', i.e. acting as a cathode, the other is 'off', i.e. acting as an anode. This configuration ensures that a clean anode surface is always available and, thus, provides the long term process stability required in industrial systems. Pairs of magnetrons can also be driven in the mid-frequency AC mode, which typically operates at frequencies of the order of 40kHz [25,26,27]. In this mode, the current to the magnetrons varies sinusoidally throughout the pulse cycle,

and again each magnetron acts alternately as a cathode and an anode.

The combination of long term (up to 300 hours [25]) process stability, high quality defect free films and commercially viable deposition rates provided by both mid-frequency AC and pulsed DC sputtering has led to their adoption in a number of applications, particularly large area applications, which depend on dielectric thin films. These applications include low emissivity and solar control coatings on architectural or automotive glazing [28,29]; anti-reflection/anti-static coatings on glazing or displays [30,31]; transparent conductive oxide coatings for displays, touch panels or photovoltaics [29,32], solar absorbers [33] and electrochromic windows [34].

### 3. The impact of pulsed processing on the film structure and properties

The impact of pulsed processing at the target (and at the substrate [17,35]) has been well documented. In the case of dielectric coatings, the ability to suppress arcing has been shown by the present authors to result in fully dense, defect-free films with enhanced structures [9,36,37], enhanced durability, enhanced optical properties and reduced surface roughness [23,38]. Other researchers have shown higher deposition rates for dielectrics in a pulsed mode, compared to RF sputtering [39], and have demonstrated the ability of pulsed magnetron sputtering to produce crystalline  $\text{TiO}_2$  films at low substrate temperatures and without the need for post-deposition annealing [40,41]. Pulsed sputtering has also been found to be beneficial in the deposition of aluminium-doped zinc oxide [42], tin oxide [26], diamond-like carbon [43] and indium tin oxide [44,45].

However, the advantageous deposition conditions offered by this process have also been exploited during the deposition of other materials where arcing is not considered a problem. For example, figs. 4a and b are SEM micrographs of the fracture sections of  $\text{CrB}_2$  coatings deposited by continuous DC and pulsed DC magnetron sputtering, respectively [46]. The continuous DC coating has a columnar structure. The tops of the columns are clearly visible and the surface is relatively rough. In contrast, the pulsed DC coating is exceptionally dense and smooth. These coatings were sputtered directly from blended powder targets consisting of chromium and boron. This is a technique pioneered by the authors, which has proved particularly useful for the deposition of multi-component coatings. Materials deposited using this technique include a wide range of transparent conductive oxide coatings [47], copper indium diselenide (CIS) [48] and copper oxide/aluminium oxide [49]. Many of these blended targets will not sputter in a continuous DC mode, but the discharges ignite readily in a pulsed DC mode, providing a new, highly flexible technique for investigating candidate materials and identifying optimum compositions.

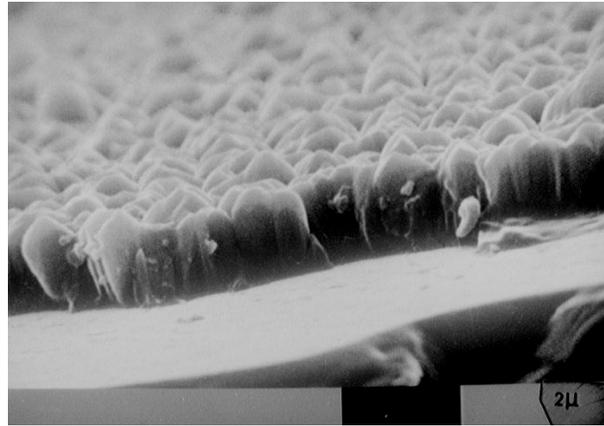


Fig. 4a:  $\text{CrB}_2$  coating deposited by continuous DC sputtering [46].

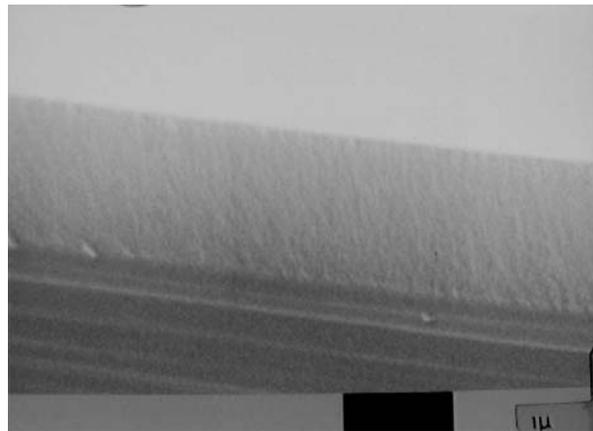


Fig. 4b:  $\text{CrB}_2$  coating deposited by pulsed DC sputtering [46].

Another material which has been investigated is titanium nitride, TiN [50]. Many components are coated with this to provide a wear resistant surface and extend the life of, for example, cutting tools. TiN is a well-characterised material that can be readily deposited by a number of CVD and PVD techniques. Despite this, significant structural and tribological enhancements have been obtained through the use of pulsed processing. For example, significant reductions in the coefficient of friction have been observed in non-lubricated thrust washer tests. In addition, fig. 5 compares the relative performance of twist drills coated with TiN by continuous DC sputtering, pulsed DC sputtering and low voltage electron beam evaporation (LVEB) [50]. The drills were tested by repeatedly drilling holes into steel plate until catastrophic failure occurred. The results indicate that the pulsed DC coated drills out-performed the continuous DC coated drills and the LVEB coated drills by factors of 2.5 and 1.6, respectively, based on median tool life values. This improvement in performance has been attributed to the structural and topographical modifications occurring

through the introduction of pulsed processing during deposition.

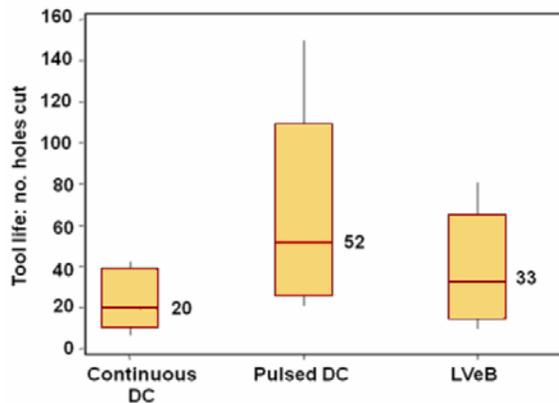


Fig. 5. Drill test results for DC, pulsed DC and low voltage electron beam evaporated (LVeB) TiN coatings deposited onto 6.35mm HSS twist drills, showing the range, median tool life and inter-quartile range box [50].

#### 4. Characteristics of pulsed discharges

Pulsed magnetron discharges are complex, due to the transient features in the voltage waveform and the spatial variations in the magnetic field and plasma density. Intrusive and non-intrusive time-averaged and time-resolved diagnostic techniques have all been applied with different degrees of success to characterise these discharges. Early Langmuir probe studies [15, 51-53] established that the time averaged electron temperature,  $T_e$ , and density,  $N_e$ , were greater in pulsed discharges, compared to continuous discharges, which was attributed to stochastic heating of the electrons by the oscillatory nature of the sheath at the target. These factors, in turn, resulted in greater fluxes of charged particles being transported to the growing film, thereby providing potentially enhanced deposition conditions (depending on the film/substrate combination). Time-resolved Langmuir probe studies have provided much more detail on the temporal evolution of  $T_e$  and  $N_e$  [54,55]. It has been observed that there is a short (~500ns) burst of 'hot' (~10eV) electrons away from the target at the start of the pulse-on cycle. For the remainder of the on cycle,  $T_e$  and  $N_e$  are modulated by the driving voltage waveform. Then, at the on-to-off transition, there is a further burst of hot electrons, followed by some decay of the plasma in the off period. However, decay times for these discharges (a few tens of microseconds [56]) are greater than the duration of the off period (1-10  $\mu$ s), thus, the plasma does not 'reignite' at the beginning of each new on cycle. Examples of time-resolved Langmuir probe measurements are presented in fig. 6. The significant transients in  $T_e$  and  $N_e$  at the on/off and off/on transitions immediately imply that the pulse frequency is likely be an important factor in determining the characteristics of a given discharge and, therefore, an important factor in determining the film

structures and properties, which has indeed been observed by a number of researchers e.g [57,58,59]. Other diagnostic techniques, including 2-D optical imaging [60], optical emission spectroscopy [55,61], emissive probes [62,63] and B-dot probes [64,65] have all provided results which correlate well with these findings.

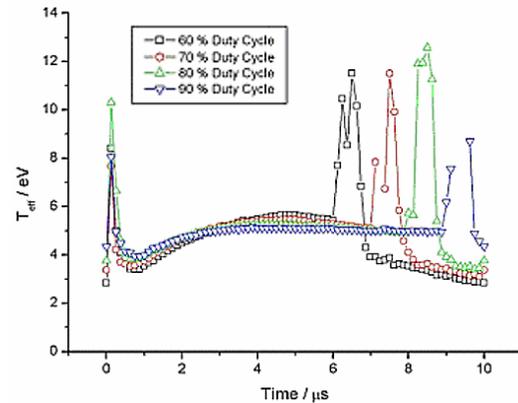


Fig. 6. Langmuir probe results showing the variation in the electron temperature with the duty cycle for a 100kHz pulsed DC discharge [55].

Another important diagnostic technique for pulsed discharges is energy-resolved mass spectrometry [66]. Referring back to fig. 1, it can be seen that the typical target voltage waveform can be divided into three sections: the pulse on phase; the positive voltage overshoot at the beginning of the off phase; and the steady-state pulse off phase. An important finding from emissive probe studies was that the plasma potential remains the most positive potential in the system, even during the off phases [62,63]. During the on phase, the plasma potential sits just above ground, as in a DC discharge. At the on-to-off transition, the target potential can reach positive potentials of several hundred Volts for a very short period, depending on the pulse frequency, but the plasma potential will still remain above this value. This has important implications for the ion energy distribution functions (IEDF) in these discharges. Fig. 7 gives a typical example of the argon IEDF at 100kHz pulse frequency, 50% duty, 500W average power [67]. Three distinct populations of ions can be discerned. During the pulse on phase, a single population of ions is created, with energies similar to a DC discharge (2-5 eV). The mid-energy peak relates to ions created during the steady-state pulse off period, when the target potential will be a few 10s of volts positive and the plasma potential will sit at a few volts higher than this, and ions will be created with energies in the 20-25 eV range. Finally, there is a high energy peak, which relates to ions created during the positive voltage overshoot period, when the target potential (and thus the plasma potential) can briefly reach several tens, or even hundreds of Volts positive. The relatively narrow distribution of energies in the low and medium populations is due to the constant magnitude of the plasma potential during these periods,

compared to the varying potential (and broader energy distribution) during the overshoot period. Time and energy resolved measurements have confirmed the time periods during which each population of ions is created [68].

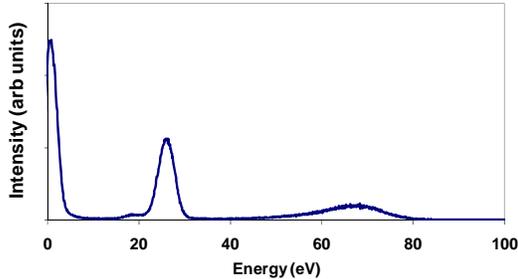


Fig. 7. Argon ion energy distribution function for a 500W discharge at 100kHz pulse frequency, 50% duty [67].

More extensive mass spectrometry studies have shown that at higher pulse frequencies, the peak energy of each population shifts to higher energies and also that the higher energy population becomes a greater proportion of the total IEDF [68]. Not surprisingly, thermal probe studies have shown that there is an associated rise in the substrate thermal flux with increasing pulse frequency, as shown in fig. 8 [69]. This figure includes the thermal flux recorded in both the DC and 40kHz AC modes, for comparison. The flux in the DC mode is noticeably lower than all of the pulsed data, whereas the AC value is approximately equivalent to the flux at 100kHz, 50% duty in the pulsed DC mode.

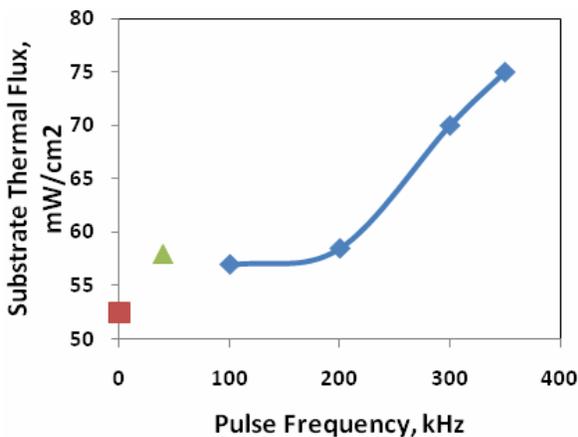


Fig. 8. Variation in the substrate thermal flux with pulse frequency (50% duty). Equivalent DC and 40kHz AC values are shown as a square and a triangle, respectively [69].

## 5. High power impulse magnetron sputtering (HIPIMS)

HIPIMS is a relatively new development in the pulsed sputtering field [70]. Sometimes also referred to as

HPPMS (high power pulsed sputtering) or MPP (modulated pulse power), this technique is attracting considerable interest, due to its ability to generate a highly ionised metal flux (up to 90% has been reported, but this figure varies significantly depending on the target material [71]), thus giving the benefits of cathodic arc evaporation without the problem of droplets. The HIPIMS waveform is very different to the pulsed DC one, as shown in fig. 9. Pulse frequencies are of the order of a few Hz to 1kHz. Pulse on times are relatively long (100-400  $\mu$ s), but because of the low pulse frequencies, duties are very low (1-5 %). However, during the on pulse extremely high peak currents ( $\sim$ 1000A) and powers ( $\sim$ 1MW; power densities  $>$   $1\text{ kW cm}^{-2}$ ) can be achieved [72]. These high peak powers in turn create plasma densities two orders of magnitude greater than conventional magnetron discharges ( $10^{19}\text{ m}^{-3}$ ), resulting in significant ionisation of the sputtered species [71].

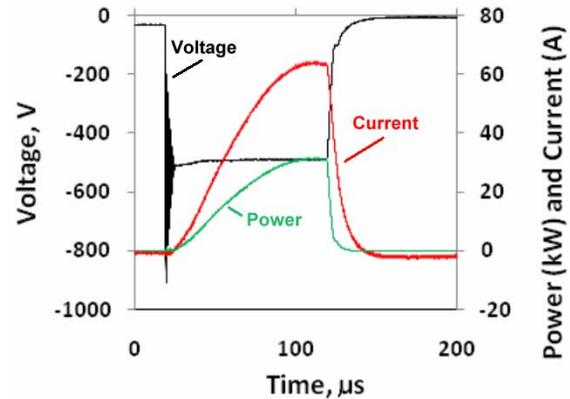


Fig. 9. Current, voltage and power waveforms obtained for the Trumpf HMP/1 HIPIMS power supply [79].

Understanding of the HIPIMS discharge and its potential is developing as more groups become involved in the study of this process. To date, literature has been published which suggests that deposition rates are lower in this mode, compared to continuous DC rates e.g. [71,73], and a model has been proposed to account for this [74]. However, more recent results have shown improvements in this respect [75,76]. Helmersson found reduced hysteresis behaviour when depositing alumina in this mode, and showed the formation of crystalline structures at relatively low substrate temperatures [77]. Ehasarian, *et al.* utilised the high ion currents in the HIPIMS mode for enhanced substrate etching, leading to improved coating adhesion and reduced corrosion rates for CrN-based coatings [78]. Sarakinos, *et al.* produced  $\text{TiO}_2$  coatings with higher refractive indices and densities and lower surface roughness values in this mode, compared to DC sputtered coatings [73] Finally, the present authors have demonstrated that the substrate thermal flux in the HIPIMS mode is significantly lower in comparison to the continuous DC and pulsed DC modes, opening the door to

deposition onto thermally sensitive substrate materials [79].

## 6. Summary

Pulsed magnetron sputtering is an enabling process for the deposition of dielectric materials and, as such, finds many industrial applications. In addition, the advantageous deposition conditions when operating in this mode can also be exploited during the deposition of many other materials, including titanium nitride. Pulsed magnetron plasmas are complex and difficult to characterise. However, time-resolved diagnostic studies have confirmed that the characteristics are very strongly related to features in the driving voltage waveform. For example, the positive voltage overshoot at the start of the pulse on period in the pulsed DC mode results in the creation of highly energetic ions, not present in a DC discharge. The flux of these ions increases with pulse frequency, contributing to a corresponding increase in the substrate thermal flux.

HIPIMS is a new development in pulsed processing that extends the process envelope for surface engineers. The highly ionised metal flux in this mode is beginning to be utilised for substrate etching and the deposition of 'high temperature' structures at reduced substrate temperatures. The low substrate thermal flux also offers the potential for deposition onto thermally sensitive substrate materials.

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