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Influence of substrate conditions on the temporal behaviour of plasma parameters in a pulsed dc magnetron discharge

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Abstract. Using time-resolved optical emission spectroscopy and Langmuir probing, the effect of substrate bias (and the absence of the substrate) on the energetics and concentrations of the plasma species at different phases of the pulse have been investigated in a bi-polar unbalanced pulsed dc magnetron. The discharge was operated in a range of frequencies, 25-100 kHz, and duty cycles, 60–90%, at a constant Ar pressure of 0.66 Pa. In the presence of an electrically grounded substrate at the transition from discharge on to off (when the plasma potential is raised to values over +150V relative to ground), we have detected a short-lived burst in optical emissions from transitions in Ar and Ti (of duration 200 ns) in the plasma bulk. We also detect an associated elevation in the effective electron temperature measured with the Langmuir probe ($T_{\rm eff}$ > twice that during the rest of the cycle). This phenomenon, we believe, is due to the liberation and increased confinement of electrons emanating from the substrate due to local ion bombardment. With an electrically floating substrate there is a much weaker associated optical flash, and none in the absence of the substrate. The Langmuir probe results also show that in the on phases of the pulse, a general increase in effective electron temperature and density is observed with decreasing frequency and duty cycle, i.e. increased reverse times. The implications of the observed transient bulk heating of electrons on the pulsed sputter deposition process are briefly discussed.

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1. Introduction

Pulsed magnetron sputtering [1] in the mid frequency range (20–350 kHz) has become a valuable industrial technique for the deposition of engineering quality thin films and coatings, including dielectric materials [2]. The success of the general technique lies in the fact that when operated in reactive gases (e.g. O_2 and N_2) any positively charged insulating material accumulated at the cathode is discharged by electrons in the off time of the pulse [3], so relieving arcing events. Two basic configurations of power delivery are utilized, the uni-polar and bi-polar modes [4]. The former is characterized by the discharge voltage V_d returning to ground potential in the off time, while with the latter, V_d has a positive voltage (usually 20–50 V) above ground in what is often termed the reverse phase.

In some pulsed configurations, there is a distinct positive voltage overshoot in V_d during the transient period between on and reverse phases, with V_d reaching voltages over +300 V for periods <200 ns [5]. It has been found that these overshoot executions in V_d greatly affect the plasma potential V_p throughout the plasma bulk, raising V_p to many hundreds of volts above ground (V_p maintains several volts above V_d) [5]. Energy-resolved mass spectroscopy [6]–[9] has shown that this in turn leads to the presence of high-energy ions (Ar⁺ and sputtered ionized species) impacting grounded surfaces, i.e. the chamber walls and the substrate (depending on the chosen substrate bias configuration). The measurement of the temporal evolution of the plasma parameters in the pulsed magnetron discharge is now recognized as important in understanding the fundamental discharge processes (see the review [10]). Electrical probe diagnostic techniques that have been used to good effect include time-resolved single Langmuir probes (e.g. [11]–[15]), double probes [16] and emissive probes [17], which all yield information on the temporal or spatial variation of the electron (ion) density, $n_{\rm e}$, electron temperature, $T_{\rm e}$, (electron energy distribution function, eedf) and plasma potential, Vp. However, although electrical probes can yield local information on the plasma parameters, by their nature they are invasive. In a pulsed magnetron plasma, their operation can be affected by factors such as the magnetic field [15], the transient electric fields [5, 18], material deposition [19] as well as other phenomena.

One non-invasive technique now being utilized for such plasmas is time-resolved optical emission spectroscopy (OES). This yields information on the time evolution of the species

present in the discharge by studying emission lines from both the carrier gases and sputtered materials. Time-resolved OES has been performed in both uni-polar and bi-polar magnetron plasma configurations [8, 10, 12], [20]–[25]. However, the observation of line intensities from spontaneous plasma emission is difficult to interpret quantitatively, for instance to determine the electron temperature or density, particularly at low pressure. Collisional radiative models (developed by solving the Boltzmann equation for the eedf in planar dc magnetron discharges) [26]–[28], Boltzmann plots [23] and line intensity ratios [20] have all been employed in an attempt to quantify these OES measurements.

In many of these reported cases, the pulsed voltage waveform either did not exhibit the large positive overshoot potential characteristic of our work with the Pinnacle Plus bi-polar device [9, 18], with the exception [8], or the authors did not report on the effect of this large transient on the optical response (and therefore energetics of the plasma). In [8], a +250 V overshoot of the cathode potential is seen at the transition from on to off phase of the pulse, with corresponding peaks seen in the measured optical signals. This is in agreement with our preliminary OES results, which suggest the positive overshoot of V_d (which causes a similar excursion in V_p) leads to enhanced excitation in the plasma due to electron release at plasma boundaries (walls and substrate). This paper details our investigation of this phenomenon, with a more careful study of the effect of the bias potential of the substrate during pulsed operation and the resulting level of electron excitation of the plasma species (i.e. heating of the plasma). To do this, we use both time-resolved OES and Langmuir probe measurements as complementary techniques.

2. The experimental arrangement

2.1. The plasma discharge

The discharge was maintained in a stainless steel cylindrical vacuum chamber 60 cm in diameter and 75 cm in length. Figure 1 shows a schematic diagram of the experimental arrangement including the magnetron target (with magnetic field lines), the substrate position as well as the Langmuir probe and optical collimator line-of-sight measurement position. The chamber was pumped to a base pressure below 1 mPa via a 1000 litres s^{-1} turbomolecular pump (Leybold Turbovac 1000) backed by an 11 litres s^{-1} rotary pump (BOC Edwards E2M40). A VTech150 series unbalanced magnetron, built by Gencoa Ltd, is mounted in the top of the chamber with its axis orientated vertically downwards. The magnetron has a water cooled, circular planar titanium target 150 mm in diameter surrounded by a shielding plate. During operation, the chamber pressure was monitored by a capacitance manometer pressure gauge (MKS Baratron[®]) situated near the magnetron. Operating gas, in this case Ar, can be fed into the chamber via MKS Mass-Flo Controllers (MFCs). The pressure was regulated via a feedback loop between the Baratron and the MFCs controlled by a Type 146C Cluster Gauge using user defined set points. An operating pressure of 0.66 Pa was maintained throughout this study. The magnetron was powered by a Pinnacle Plus[®] pulsed dc power supply (from Advanced Energy Inc.). It has a single output of up to 5 kW power with pulse frequencies of 0-350 kHz in 5 kHz steps. It allows reverse (off) times from 0.4 μ s to a maximum of 5 μ s with the limit that the duty cycle (α) be always $\geq 50\%$ of the total period (τ). The reverse voltage is fixed at approximately 10% of the sustaining voltage. The power supply was regulated in constant power mode with a nominal (time-averaged) power of 400 W used throughout. Pulse frequency was set at 100 kHz with a 60% duty cycle during



Figure 1. Schematic of the discharge chamber and experimental setup including the magnetron (with magnetic field lines) and the substrate position together with the positioning of the Langmuir and optical probes.

the investigation into the effect of the condition of the substrate, giving a $6 \mu s$ on phase and a $4 \mu s$ reverse phase. A 150 mm × 150 mm square aluminium substrate, typically used for film deposition, was positioned parallel to the target surface at a standard deposition distance [29] of 125 mm.

The discharge voltage (V_d) and current (I_d) waveforms were determined at an intermediary test box situated between the target and the power supply and were recorded on a digital oscilloscope. V_d was measured using a ×100 voltage probe (Tektronix Ltd model P5100) and I_d was determined using a current probe (Tektronix Ltd model TCP202). We define the time t = 0as the point where V_d passes through zero, between the off and on phases. A trigger TTL signal from V_d on the test box was taken via a delay generator (Stanford Research Systems, DG535). Figure 2 shows an example of the typical characteristic discharge current and voltage waveforms.

2.2. The optical emission spectroscopic system

Optical emissions were recorded via an optical 'probe' positioned inside the chamber. The probe head consisted of an optical fibre connection, a movable lens, a 45° mirror and a collimating tube. The collimating tube enabled continuous use without sputtered material depositing on to the optical components. Use of the collimating tube resulted in the viewing area of the plasma



Figure 2. The discharge current (I_d) and voltage (V_d) waveforms for a 100 kHz pulse frequency with a 4 μ s reverse time (60% duty cycle). In the transition between on and reverse phases the discharge voltage rises to over +150 V.

being that of a truncated cone through the width of the plasma, with end diameters of 6 and 40 mm. The plane of focus of the 'probe' was parallel to the target surface at a distance of 90 mm from the target. As such, the optical measurements correspond to a region of plasma directly above the substrate surface and outside of the magnetic trap region. We do not investigate the full extent of the plasma here; instead we concentrate the optical and Langmuir probe measurements (described below) to only this one region of the plasma above the substrate. The viewing area is such that diffusion of species into and out of the viewing area will be approximately equal, hence we do not expect a significant net change in neutral atom density within the viewing area during a pulse period.

The light from the optical fibre was focused on to the entrance slit of a 25 cm focal length fully automated imaging spectrograph (L.O.T Oriel MS260i). The spectrograph was operated with a 600 lines mm⁻¹ grating and a 50 μ m slit giving a typical resolution of approximately 0.3 nm. Mounted at the exit point of the spectrograph was an Andor iStar DH520 ICCD (Intensified Charge Coupled Device) with 1024×256 , $26 \,\mu m^2$ pixels. The detector can be internally cooled to -20° C and electronically gated with an external TTL trigger for time-resolved measurements. The ICCD and the spectrograph were both fully controlled by the imaging software, including wavelength calibration for spectroscopy. Two specific regions of the emission spectrum were selected, each about 100 nm wide. The first emission region from 330 to 430 nm has many Ti emission lines, including the strong lines at 398-400 nm. The second region from 720 to 820 nm contains many of the Ar emission lines corresponding to the $4p \rightarrow 4s$ transitions. Typical spectra from these wavelength regions can be seen in figure 3(a). Excitation of the Ar 4p levels (denoted 2p1 to 2p10 in Paschen's notation) has been extensively studied elsewhere and is summarized, for example, in the topical review by Donnelly [30] and references therein. Chilton et al [31] and Boffard et al [32] report measured electron impact excitation cross-sections for direct and cascade excitation as well as stepwise excitation from the 4s metastable states. These measured cross-sections agree well with the computed cross-sections of Bartschat and Zeman [33]. These cross-sections show that of the ten 4p energy levels, the $2p_1$ level has the smallest contributions





Figure 3. (a) Example emission spectrum for the wavelength regions 330–430 nm and 720–820 nm. (b) Example Langmuir probe $I-V_{\rm B}$ characteristics shown for one point in time in the on phase (----) and one point in time in the reverse phase (----) during pulsing at 100 kHz.

Table 1. Transition data and energy levels for the Ti 398.1 nm and Ar 750.4 nmemission lines.

Species	Wavelength (nm)	Energy levels $E_k - E_i$ (eV)	Transition
Ti I	398.1	3.11–0.00	$\begin{array}{c} 3d^2 \ 4s^2 - 3d^2({}^3\mathrm{F}) \ 4s \ 4p({}^1\mathrm{P}^{\mathrm{o}}) \\ 3s^2 \ 3p^5({}^2\mathrm{P}_{1/2}) \ 4p - 3s^2 \ 3p^5({}^2\mathrm{P}_{1/2}) \ 4s \end{array}$
Ar I	750.4	13.48–11.83	

from both cascades and metastables. Hence, emission lines from this level, e.g. the 750.4 nm line, are often used for things such as actinometry [34]. Here, it is assumed that direct excitation from the ground state is the dominant excitation method and as such the 750.4 nm line is indicative of the behaviour only of electrons with energies >13.48 eV. This assumption should be used with caution however; as modelling of excited Ar levels in the magnetized region of magnetron discharges [27] shows that if the ionization fraction and discharge current are high then stepwise and cascade contributions to the $2p_1$ level can become important. However, even under the model conditions of [27], stepwise contributions from lower lying energy states contribute only about 20% of the production of the $2p_1$. Hence here, and following the same assumptions in other optical studies of magnetron discharges [12, 20], we will assume the 750.4 nm Ar line exhibits similar behaviour to the high energy part of the eedf. We also observe a titanium emission line at 398.1 nm as a guide to excitation due to the lower energy electrons in the distribution, as the upper level of this transition is at an energy of around 3 eV. A summary of the energy levels and transitions for these emission lines is presented in table 1.

2.3. The Langmuir probe system

A cylindrical Langmuir probe, 0.15 mm in diameter and 15 mm in length, was inserted into the plasma along the centre line of the discharge at a distance of 90 mm from the target. Probe

characteristics were obtained using an automated ESPion[®] acquisition system (Hiden Analytical Ltd). Example probe current–voltage $(I-V_B)$ characteristics can be seen in figure 3(b). The ESPion acquisition unit is a computer controlled pulsed plasma analyser which can measure time-resolved probe characteristics, with a time resolution of 500 ns, via an external triggering TTL signal taken from the power supply voltage waveform. The eedf $g_e(\varepsilon)$ (which we assume is not a Maxwellian [35]), with $\varepsilon = eV$, was obtained from the numerically differentiated second derivatives of the probe characteristics. The electron density (n_e) and the effective electron temperature (T_{eff}) were calculated from the integrals of the eedfs as follows.

$$n_{\rm e} = \int_0^\infty g_{\rm e}(\varepsilon) \mathrm{d}\varepsilon \tag{1}$$

$$T_{\rm eff} = \frac{2}{3} \langle \varepsilon \rangle = \frac{2e}{3n_e} \int_0^\infty \varepsilon g_{\rm e}(\varepsilon) \,\mathrm{d}\varepsilon \tag{2}$$

The plasma potential V_p was estimated from the crossing point of the second derivative of $g_e(\varepsilon)$, namely where $g''_e(\varepsilon) = 0$ [36]. From our knowledge of the magnetron, we can estimate the characteristic response times (τ_{pe} and τ_{pi}) of the electrons and ions in the probe sheath, given by the inverse of the electron and ion plasma frequencies, ω_{pe} and ω_{pi} , respectively. Typically, in our plasma we have $\tau_{pe} = 1/\omega_{pe} \sim 5 \times 10^{-10}$ s and $\tau_{pi} = 1/\omega_{pi} \sim 1.5 \times 10^{-7}$ s. The latter is faster than many of the transients in the driving waveform V_d (and therefore the plasma potential V_p , see [17, 18]), so we assume the probe method is valid in the pulsed mode.

3. The results and discussion

3.1. Effect of substrate condition

Figures 4, 5 and 6 show the electron density, effective electron temperature and plasma potential respectively, measured using the Langmuir probe for three substrate conditions; namely with no substrate present, with an electrically floating substrate and with a grounded substrate. In the latter two cases the position of the probe was 35 mm in front of the substrate. From figures 4 and 5, it is clear that there is an increase in n_e and T_{eff} (over the cycle) associated with the floating substrate condition. Indeed, in the case of n_e , an increase of 100% is observed. The reflecting nature of the boundary to electrons with energy below the equivalent of the floating potential leads to higher densities than at an absorbing boundary. At both transitions between on-off and off-on, we find (using equation (2)) a peak in $T_{\rm eff}$ for all substrate cases. However, the effect is weaker in the absence of the substrate. Later we argue that the presence of hotter electrons during the on-off transitions is enhanced due to secondary electrons released at a substrate; clearly there is some effect however from the more remote walls. These peaks may be due to the presence of hot or beam-like electrons generated specifically at the main discharge voltage transients. The generation of hot electrons at the off-on transition is discussed in more detail in [11]. The presence of hot electrons at the transition from the on-off phase of the pulse has already been observed in the same system [11, 15]; however when reported it was thought this signature may be due to distortion in the probe characteristics. These results and those in the optical emission detailed below indicate that energetic electrons do in fact exist at certain periods of the pulse.



Figure 4. Temporal evolution of the electron density n_e without a substrate (- \Box -), with a grounded substrate (- Δ -) and with a floating substrate (- \bigcirc -). The pulse frequency was 100 kHz with a 60% duty cycle.



Figure 5. As for figure 4 for effective electron temperature T_{eff} .

As seen in figure 6, the presence of a floating substrate leads to more negative plasma potentials in the bulk during the on time and more positive potentials during the reverse time. A grounded substrate leads to an adjacent plasma potential just above ground to self-consistently restrict electron loss to be no greater than net ion loss. Figures 7 and 8 show the optical emission from the 750.4 nm line in Ar and the 398.1 nm in Ti for the same set of conditions as for the Langmuir probe measurements. It is clear that the floating substrate condition leads to more intense lines, confirming the trends in the Langmuir probe results that the plasma is denser and more energetic with a partially electron reflecting boundary. In the case of the Ar emission, we



Figure 6. As for figure 4 for plasma potential V_p . The peak values represented by the dotted lines at $t = 6 \,\mu s$ were not measured here but inferred from previous emissive probe measurements [19, 23] and are a guide to the eye only.



Figure 7. As for figure 4 for the argon emission line intensity at 750.4 nm. There is a pronounced peak in intensity at $t \cong 6 \,\mu$ s with a grounded substrate present.

see also a peak in intensity in all three substrate cases at the start of the on time (t = 0-200 ns), which lends weight to the idea that beam-like electrons are generated in this phase as discussed in [11].

The decay time of the Ar emission line is approximately 0.4 μ s, which is distinctly faster than the 2 μ s decay time of the Ti emission line, reflecting the difference in threshold excitation energy of the upper states and hence the range of the eedf sampled by each line. No peak is observed in the Ti emission at the off-on transition, as seen in the Ar emission, possibly reflecting the high



Figure 8. As for figure 4 for the titanium emission line intensity at 398.1 nm. There is a pronounced peak in intensity at $t \cong 6 \,\mu s$ with a grounded substrate present.

energy or 'beam-like' nature of the burst of electrons observed at this transition [11]. However, for both the Ar and Ti spectral lines, a pronounced peak in the optical emission is recorded at the on-off discharge voltage transition ($t = 6 \mu s$) when a local grounded substrate is present. At this voltage transition phase of the pulse, the overshoot associated with the voltage reversal raises the target potential to high values, +150 V in this case. The electrons which were previously confined in the magnetized region are now free to flow to the target along the field lines, which we observe as a large spike in the target current trace at this time. The rapid capture of these electrons is accompanied by a very fast modification of the plasma potential distribution in order to preserve quasi-neutrality. The plasma potential, V_p , is raised to values $\geq V_d$ during this overshoot phase of the pulse [17]. This will generate a matrix sheath at a grounded surface. Plasma ions close to a grounded surface will strike this boundary with energies approaching this value, so liberating secondary electrons. This can happen during the 200 ns overshoot phase provide ions are within \sim 2 mm of the boundary, i.e. in or around the sheath. Emitted electrons are accelerated back into the discharge, executing about one excitation mean-free-path before exciting the background argon and sputtered titanium. The transit time of these sheath accelerated secondary electrons across the discharge is of the order of 100 ns or less.

Clearly, the effect and observation of electron liberation, sheath acceleration and neutral excitation is stronger with a grounded substrate located in the dense bulk plasma than that which occurs at the more remote grounded vessel walls, due to increased ion density in the vicinity of the substrate and its position relative to the measurement region. Electrons released at the remote walls will generally have to travel many excitation mean-free-path lengths before entering the region viewed by the optics or sampled by the probe and as such will loose energy via collisions in the process. However, T_{eff} is raised somewhat during this transition even in the absence of a substrate, as shown in figure 5, indicating that these liberated electrons still retain an increased energy distribution compared to the bulk plasma electrons.

It appears however that this 'injection' mechanism does not lead to a large increase in ionization of the neutrals, since n_e is not observed to rise in the period immediately after the



Figure 9. Temporal evolution of the electron density n_e for a pulse frequency of 100 kHz at duty cycles of 60% (- \Box -), 70% (- \bigcirc -), 80% (- \triangle -) and 90% (- \bigtriangledown -) with a grounded substrate.

voltage reversal. However, we do lose confidence in the density measurement determined from Langmuir probe I-V characteristics during the fast transient phase (when V_d swings by up to 1 kV in 100 ns) and overshoot period, as they suffer from offset displacement currents and because the overshoot period is typically shorter than the 500 ns time resolution of the Langmuir probe. As a result, n_e measurements during the overshoot period are not presented in figure 4 (and figure 9, see subsection 3.2). We do however have more confidence in T_{eff} as it is derived from the second moment of $g(\varepsilon)$, which is weakly dependent on probe current shifts. At a floating substrate an ion matrix sheath will not form, since on a time scale governed by the electron plasma frequency the floating potential, V_f , of the substrate will follow the change in V_p (the difference between V_f and V_p , governed by T_{eff} [18]). The effect of the substrate potential on the nature of the eedf and the reflection of electrons back into the plasma in the pulsed magnetron has been discussed in detail [37, 38]. During the times of high plasma potential observed in this study, energetic electrons that are normally lost from the discharge (and result in fast cooling of the electron distribution function in the off time) are reflected back into the plasma. This will also contribute to an increase in the optical emission and values of T_{eff} measured with the Langmuir probe.

3.2. The effect of duty cycle and pulse frequency

In this part of the study, the substrate was present and maintained at ground potential. The pulse frequency and duty were varied to determine the trends in n_e , T_{eff} and optical intensity for different pulse conditions. Lieberman and Ashida [39] describe a global modal of pulse power modulated, high density, low pressure discharges. Aside from the overshoot periods of our pulse, the results here agree with a model of this type (the model uses a theoretical square wave and hence the waveform does not contain any overshoots). The model predicts that in the initial period after switch on, dT_e/dt and to a lesser extent dn_e/dt is proportional to the term P_{max} . $P_{max}(= P_{avg} \times 100/\alpha)$ is the power applied during the on time where P_{avg} is the time average



Figure 10. As for figure 9 for effective electron temperature $T_{\rm eff}$.



Figure 11. As for figure 9 for the argon emission line intensity at 750.4 nm.

power (in this case 400 W) and α is the duty cycle. Figures 9 and 10 show the measured values of $n_{\rm e}$ and $T_{\rm eff}$ with changing duty cycle. The trends observed in these figures match those expected from the model. At 60% duty, $n_{\rm e}$ and $T_{\rm eff}$ start with the lowest values (due to the increased decay time) but the rate of rise is the fastest so that by the end of the on phase they have the highest values. The effect is not a dramatic one as the total period τ is only 10 μ s, which is short compared to the time needed to reach equilibrium values (as eluded to later). These trends are also seen by Seo *et al* [14] for a similar magnetron pulsed at 20 kHz. As before, during the transient phases interpretation of the Langmuir probe is difficult, and we lose confidence in the determination of $n_{\rm e}$. The measured optical signal from the Ar 750.4 nm emission line as duty cycle is varied is shown in figure 11. It reveals an increased intensity for lower duty cycles, confirming the picture



Figure 12. Temporal evolution of the electron density n_e for a duty cycle of 90% at pulse frequencies of 25 kHz (- \Box -), 50 kHz (- \circ -), 75 kHz (- Δ -) and 100 kHz (- ∇ -) with a grounded substrate.



Figure 13. As for figure 12 for the effective electron temperature T_{eff} .

of elevated T_{eff} and n_{e} seen with the Langmuir probe. However, the increase in the observed light intensity is almost double between 60 and 90% duty, much more than that seen in either T_{eff} or n_{e} measurements. The short-lived flashes in light observed at the transitions between on and off phase are clearly seen in figure 11.

Figures 12, 13 and 14 show the effect of varying the pulse frequency (at constant duty cycle) on n_e , T_{eff} and the Ar 750.4 nm emission respectively. The previously described peak features observed at the transitions are also observed here. Similarities with the pulsed power modulated model [39] can again be seen. With the increasing length of the on time as frequency



Figure 14. As for figure 12 for the argon emission line intensity at 750.4 nm.

decreases, we can see the different time evolutions of T_{eff} and n_{e} predicted by the model. In the period just after the pulse has been turned on, there is a very sharp rise in T_{eff} up to some maximum value, which is seen here at around $5 \,\mu$ s. After this time T_{eff} falls until it reaches an equilibrium value of ~4.3 eV. On the other hand, n_{e} initially rises more slowly until it reaches its equilibrium value, after around $15 \,\mu$ s in this case. This effect is not clearly seen at high frequencies (as in the previous duty cycle study at 100 kHz) as the on phase is not sufficiently long for the equilibrium values to be reached. The peak electron temperature and density values show a small rise with decreasing frequency. However, figure 14 shows a large difference over one cycle in optical emission between 25 and 100 kHz (a factor 3 increase). Accompanying this large increase in optical emission is similarly large increase (more negative) in the measured values of V_{d} as pulse frequency decreases.

The discharge voltage $V_{\rm d}$ at the start of the on phase, for example, increases from $-340\,{\rm V}$ at 100 kHz up to -420 V at 25 kHz. Electrons enter the magnetized region of the plasma across the cathode sheath, acquiring an energy $\varepsilon = eV_d$, where they are confined by the magnetic field lines. Electrons that undergo collisions at the edge of the magnetized region (the border between the closed magnetic field lines and the open field region) can escape the closed field lines and travel into the area viewed by the optical system. Electrons with higher energy can more easily escape the magnetized region [26]. As a result, the high energy portion of the eedf in the magnetized zone decreases as V_d increases, as modelled by Guimarães et al [26]. Beyond this region, including the viewing area of our optical measurements, the high energy portion of the eedf must therefore increase with increasing V_d . It is also possible for the high-energy primary electrons to enter the viewing area along the open field lines created by the unbalanced magnetic configuration at the edge of the discharge, as the optical measurements are line of sight. It is therefore not unreasonable that combined with the slight increase in n_e and T_{eff} as frequency drops, the optical signal can show a much greater increase. To show these temporal variations in the plasma density, effective electron temperature and also the optical emission, these parameters have been plotted together with discharge current I_d in figure 15. Here, we show the particular example of 25 kHz, where these trends are most clearly seen. The vertical axes have been scaled



Figure 15. The combined temporal evolution of target current I_d (—), electron density $n_e(-\Box)$, effective electron temperature T_{eff} (- Δ -) and the 750.4 nm argon emission line intensity (-O-) at pulse frequency of 25 kHz with a 90% duty cycle.

to fit the data conveniently. During all of the cycle there is a strong correlation between T_{eff} and the optical intensity and with trends in I_d . The trends in n_e identified are somewhat different from I_d which indicates perhaps the current is maintained by an electron group un-detected by the probe method.

There are a number of factors in the bi-polar pulsed mode that can affect the conditions of a growing film at the substrate, depending on the applied electrical bias of the substrate or the insulating nature of the film. For instance, at a grounded surface, during the discharge voltage overshoot (on-off), high-energy ions (in our case up to at least 150 eV) will bombard the surface. As we have seen, these lead to enhanced electron emission, but also concurrently there must be some re-sputtering of the film. If the surface is electrically isolated, the difference between the floating and plasma potential remains relatively small and the above effects are minimal. However, it is clear from both Langmuir probe and OES measurements there is a short-lived (200 ns) enhancement in effective electron temperature in the transient periods between both pulse on to off and off to on. This enhancement will, as a consequence, lead to greater ion fluxes, Γ_i , and energy fluxes, $E_i\Gamma_i$, to the substrate as discussed and quantified in [6], since $\Gamma_i \propto T_e^{1/2}$ and $E_{\rm i}\Gamma_{\rm i} \propto T_{\rm e}^{3/2}$. The results here also show that pulsing the discharge also changes to some degree the overall electron density and temperature and therefore Γ_i and $E_i\Gamma_i$. For instance, the Langmuir probe results (backed-up qualitatively by the OES trends) do suggest that by lowering the frequency (at constant duty) or reducing the duty cycle, the flux or energy flux of ions to a substrate can be increased. This confirms our previous mass spectrometric and Langmuir probe findings [6].

4. Conclusions

Using time-resolved Langmuir probe measurements and OES we have studied the behaviour of the plasma at a fixed position in a pulsed dc magnetron with variation in the conditions at

a substrate (namely its bias and removal). We have found using the Langmuir probe that at the transitions from off to on there is a short-lived increase in the effective electron temperature, irrespective of substrate condition, which is observed in the optical signal (Ar 750.4 nm) as an intensity peak. We attribute this to the beam-like electrons accelerated at the target by the expanding ion sheath, as discussed in [11]. During the on to off transition in the discharge voltage, the effective electron temperature is also seen to rise substantially, particularly in the presence of a grounded substrate. Here, we also see a peak or flash in the optical emission, however only with the presence of a grounded substrate. We argue that the observed phenomenon is enhanced due to the release of secondary electrons at a grounded substrate which excite the background gas as the plasma potential reaches high positive values. There is also some short-lived electron heating in this period without the substrate and with a floating substrate due to electron release from the remote walls. The probe results for varying pulse frequency and duty also indicate that increased ion fluxes to a substrate in the on times can be achieved by increasing the off time for a fixed pulse period, i.e. by decreasing the duty cycle, or by reducing the pulse frequency for a constant duty cycle.

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