Characterization of pulsed dc magnetron sputtering plasmas

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New Journal of Physics 7 (2005) 90
Received 12 January 2005
Published 6 April 2005
Online at http://www.njp.org/
doi:10.1088/1367-2630/7/1/090

Abstract. Pulsed dc magnetron reactive sputtering of dielectrics provides a deposition process without arcing. The deposition process is usually carried out with pulsing frequencies in the range 10–350 kHz and duty cycles in the range 50–90%. The operating conditions are typically optimized empirically and are critically dependent on the properties of the pulsed plasma in the immediate vicinity of the magnetron. We show how a combination of time-resolved Langmuir probe measurements and time-resolved optical emission spectroscopy can be used to characterize the pulsed magnetron plasma and gain insights that can only be obtained conclusively by correlating the results obtained by both techniques. The pulsed dc sputtering of Al and Ti targets and the reactive sputtering of their oxides were used as examples in our experiments. Our experiments were carried out at total pressures in the range 0.4–1.3 Pa in either pure Ar (‘metallic’ mode) or in Ar–O₂ mixtures (‘oxide’ or ‘reactive’ mode) with mixing ratios from 1:1 to 1:4.
1. Introduction

Pulsed dc magnetron sputtering is a well-developed deposition technique for coatings and thin films used in industrial applications [1]–[7]. Pulsed power as opposed to dc power is used to prevent the formation of arcs. The sputter deposition of dielectrics causes the inside surfaces of a deposition chamber to be coated with non-conductive layers that accumulate electric charges from the plasma. These charges create mini- or macro-arcs which result in very uneven removal of material from the target electrode and particulate formation. These particulates are incorporated into the deposited films, which often prevent their use in high-tech applications such as thin film devices, which require uniform thin films. In addition, arcing can damage the power supply. The use of pulsed dc plasmas avoids these problems. Figure 1 shows a typical voltage sequence used in pulsed dc-reactive sputtering with a single magnetron. The power is applied to the target for a time $\tau_{on}$, the ‘on-time’ during which a negative voltage pulse of a few hundred volts is applied to the target. At the end of an ‘on-time’, the power is either switched off for a period of time $\tau_{off}$, the ‘off-time’, or, more commonly, switched to a small positive voltage (about 20 V); for that reason the ‘off-time’ is sometimes also referred to as the ‘reverse time’, $\tau_{rev}$ (which is the terminology that we will use throughout the remainder of this paper). The dielectric surfaces that are charged up during the ‘on-time’ are discharged during the ‘reverse time’. Arc-free operation requires the ‘on-time’ to be sufficiently short to avoid charge build-up that can cause breakdown and arcing and the ‘reverse time’ to be sufficiently long to fully discharge the surfaces in order to avoid charge accumulation in sequential ‘on’ and ‘reverse’ cycles. Typically, the ‘reverse’ time is about 1/10 of the ‘on-time’ [8]. Furthermore, the duration of the ‘on-time’ and ‘reverse time’ determines the lowest pulsing frequency ($f_c = 1/\tau_{cycle}$) known as the critical frequency, $f_c$, and the highest duty cycle for arc-free pulsed dc reactive sputtering [9]. Pulsed dc reactive sputtering has been widely used to deposit thin films of dielectric materials such as alumina, Al$_2$O$_3$ [10]–[13] and titania, TiO$_2$ [13]–[15], which have a smooth structure (as shown by S.E.M. studies) due to the absence of particulates created by micro-arcs [1, 12].

In recent years, time-resolved investigations of pulsed dc magnetrons operated in the metallic mode (metal deposition) were carried out using Langmuir probes to obtain the temporal variations of the electron density and the electron temperature during the ‘on-time’ and the ‘reverse time’ as well as the temporal variations of the plasma potential and the floating potential [14], [16–19]. Furthermore, time-resolved mass spectrometric studies were used to elucidate the dynamics of energetic ions in pulsed dc magnetron plasmas [20] and time-resolved optical emission spectroscopic studies revealed the temporal variation of species densities [21]–[23].

New Journal of Physics 7 (2005) 90 (http://www.njp.org/)
In this paper, we show how a combination of time-resolved Langmuir probe measurements and time-resolved optical emission studies of pulsed dc magnetron plasmas can be used to extract more detailed information regarding the temporal variations of the critical plasma parameters and plasma species that can be obtained only from probe or optical measurements. Studies were carried out for the pulsed dc magnetron sputtering of aluminum and titanium in pure argon and in argon/oxygen mixtures.

2. Experimental techniques

Our experiments were performed in a cubic reaction chamber (‘box coater’) with planar rectangular magnetrons HRC-373 or HRC-817 (BOC Coating Technology) as shown in figure 2. The magnetron was modified by replacing the centre magnets with soft iron and the side magnets with magnets that were 2.5 times stronger than the original magnets, which results in an unbalanced magnetron. The tangential component of the magnetic field above the racetrack of the unbalanced magnetron is about 40% stronger than that of a balanced magnetron. Sputtering was carried out using an aluminium target (5′′ × 17′′) or a titanium target (3.5′′ × 8′′) of a purity of 99.999%. The base pressure in the system was in the range of 3–6 × 10⁻⁶ Torr (4–8 × 10⁻⁴ Pa). The pressure during sputtering (0.4–1.3 Pa) was measured by a capacitance manometer and controlled by a throttle valve. Sputtering of Al and Ti (metallic mode) was carried out in pure argon, while reactive sputtering of Al₂O₃ and TiO₂ (oxide mode) was carried out in an Ar–O₂ mixture with a mixing ratio ranging from 1:1 (Ar:O₂) to 1:4.

The pulsed dc power was applied using a combination of an Advanced Energy MDX-10 dc power supply and an Advanced Energy Sparc-le V® pulsed generator. The dc power supply was operated in the constant current mode at currents of about 4 A. The Sparc-le V® was operated either at 20 kHz with reverse pulse widths of up to 10 µs or at 60 kHz and reverse pulse times of 3–6 µs. These operating parameters resulted in stable, arc-free plasmas. The current and voltage pulse forms were recorded with a Tektronix P5100 voltage probe and a Tektronix A6303 current probe connected to a Tektronix TDS 340 oscilloscope. The time window was chosen to record the reverse peak (‘reverse time’) and the subsequent re-establishment of the plasma.

Details of the time-resolved Langmuir probe measurements and emission spectroscopic studies and the respective data extraction procedures were discussed in greater detail elsewhere.
Figure 2. Schematic diagram of the experimental setup.

[18, 23] and only a brief summary of the pertinent features will be given here. The time-resolved plasma probe data were obtained with a home-built Langmuir probe consisting of a 4 mm long Pt wire of 0.51 mm diameter. The probe was located 7 cm from the target and 1 cm above the substrate holder with the probe tip close to the central line of the target. The probe was shielded from direct deposition. The time resolution of the Langmuir probe measurements varied between 0.2 and 0.8 µs.

The light emission from the plasma was collected with a fibre optics cable, which was also shielded from direct deposition and imaged onto the entrance slit of a SPEX model 1870 0.5 metre spectrometer equipped with a 1200 grooves/mm grating. The entrance slit was set at 100 µm to obtain an acceptable signal-to-noise ratio with a spectral resolution sufficient to resolve the Ar, Al, Ti and O emission lines. The dispersed plasma emission spectra were recorded by a Roper Scientific ICCD camera at the exit plane of the spectrometer. The emission intensities were measured every 0.5 µs with an integration time of 2 µs in the case of Al, which allows us to determine decay times down to about 1 µs. In the case of Ti, the intensities were recorded every 0.2 µs with an integration time of 0.2 µs to achieve a better time resolution. Decay times
Table 1. Summary of the Ar, O, Al and Ti emission lines and their energy levels ([37] and http://physics.nist.gov/cgi-bin/AtData/lines_form).

| Species       | Wavelength (nm) | Energy levels (Ei–Ek) | Transition                          |
|---------------|-----------------|-----------------------|-------------------------------------|
| Argon I       | 404.44          | 14.69–11.62           | \(3p^5 (^2P_{1/2}) 5p \rightarrow 3p^5 (^2P_{1/2}) 4s\) |
| Argon I       | 750.39          | 13.48–11.83           | \(3p^5 (^2P_{1/2}) 4s \rightarrow 3p^5 (^2P_{1/2}) 4p\) |
| Argon I       | 751.47          | 13.27–11.62           | \(3p^5 (^2P_{3/2}) 4s \rightarrow 3p^5 (^2P_{3/2}) 4p\) |
| Argon I       | 763.51          | 13.17–11.55           | \(3p^5 (^2P_{3/2}) 4s \rightarrow 3p^5 (^2P_{3/2}) 4p\) |
| Argon I       | 772.38          | 13.15–11.55           | \(3p^5 (^2P_{3/2}) 4s \rightarrow 3p^5 (^2P_{3/2}) 4p\) |
| Oxygen I      | 777.19          | 10.74–9.15            | \(2p^3 (^4 S) 3s \rightarrow 2p^3 (^4 S) 3p\) |
| Oxygen I      | 777.42          | 10.74–9.15            | \(2p^3 (^4 S) 3s \rightarrow 2p^3 (^4 S) 3p\) |
| Aluminum I    | 394.40          | 3.14–0.000            | \(3s^2 (^1 S) 4s \rightarrow 3s^2 (^1 S) 3p\) |
| Aluminum I    | 396.15          | 3.14–0.014            | \(3s^2 (^1 S) 4s \rightarrow 3s^2 (^1 S) 3p\) |
| Titanium I    | 398.17          | 3.11–0.00             | \(3d^2 (^3 F) 4s^2 \rightarrow 3d^2 (^3 F) 4s^p\) |
| Titanium I    | 398.98          | 3.13–0.02             | \(3d^2 (^3 F) 4s^2 \rightarrow 3d^2 (^3 F) 4s^p\) |
| Titanium I    | 399.86          | 3.15–0.05             | \(3d^2 (^3 F) 4s^2 \rightarrow 3d^2 (^3 F) 4s^p\) |

were obtained by fitting an exponential function to the recorded intensity. In some cases, a double-exponential fit was required to properly describe the data. The accuracy with which the decay times could be determined in the case of Ti sputtering ranged from \(\leq \pm 0.1 \mu s\) for intense emission lines to about \(\pm 0.3 \mu s\) for the very weak emission lines. Two spectral regions were selected for the time-resolved emission spectroscopic studies, 390–410 nm which contains emission lines of Al, Ti, and Ar and 750–780 nm which contains Ar and O emission lines. The emission lines studied here are summarized in table 1 (see also [24]). As can be seen from table 1, the minimum excitation energies for argon and oxygen are comparatively high, \(>13.15\) eV for Ar and \(>10.74\) eV for O, whereas the excitation of the Al and Ti lines requires only minimum energies of slightly more than 3 eV for aluminium and titanium. This indicates that the emission of argon and oxygen lines depends on the presence of fast electrons in the plasma.

The optical detection system was set up in such a way [23] that most of the light reaching the detector originated from a section of the densest part of the plasma from the racetrack region nearest to the fibre optics cable. The shape of the plasma area that was viewed by the optical detection system was that of a truncated cone, 4 cm in length with top and bottom diameters of 1.7 and 2.3 cm, respectively. As discussed above, the tip of the Langmuir probe was placed slightly below the plasma region that is imaged onto the optical detector and places in between the two regions of highest plasma density. Thus, the Langmuir probe analyses a plasma with a lower electron density than the plasma that is optically analysed. However, the main focus of this study was an investigation of the temporal behaviour of the plasma parameters and emission intensities during both the ‘on-time’ and ‘reverse time’ rather than their absolute values. Thus, the comparison of the electrical and optical data obtained from different, but adjacent regions of the plasma is still meaningful.

3. Results and discussion

We will present and discuss the results of time-resolved Langmuir probe and optical emission spectroscopy studies separately for the ‘reverse time’ and for the ‘on-time’ and separately for the operation of the magnetron in the metallic and oxide modes. Figure 3 shows the temporal
Figure 3. Temporal variations of the cathode voltage and current, plasma potential, plasma density and electron temperature during reactive sputtering of Al₂O₃ using 20 kHz pulsed dc power with a 10 µs off-time in the metallic mode (green symbols) and in the oxide mode (pink symbols).
Figure 4. Time-resolved emission intensities of the Ar 750 and 764 nm lines, the Al 396 nm line and the O 777 nm line measured during sputtering of an Al target in the metallic mode (upper graph) and in the oxide mode (lower graph) using a power of 1 kW, a frequency of 20 kHz, a reverse time of 10 $\mu$s and a pressure of about 0.5 Pa.

Variations of the recorded magnetron voltage and current and of the plasma parameters obtained from the Langmuir probe measurements (plasma potential, electron density and electron temperature) obtained at 20 kHz and a reverse time of 10 $\mu$s with an Al target in both the metallic and the oxide mode. The power was 1 kW and the pressure was about 0.5 Pa. Figure 4 shows the emission intensities of the Ar lines at 750 and 764 nm line together with the Al line at 396 nm obtained in the metallic mode. The same two Ar lines and the O line at 777 nm were recorded in the oxide mode. The operating conditions were the same as those used in the Langmuir probe measurements. Similar time-resolved optical data in the metallic and oxide modes were obtained for a Ti target, but with a better time resolution (figure 5). We note that the intensities of the emission lines were normalized to each other at $t = 0$ (the time when the magnetron power is reversed) for clarity of presentation. The intensities of Al and Ti lines in the oxide modes were too low for a meaningful analysis.
Figure 5. Time-resolved emission intensities for the Ar 750 and 764 nm lines, the Ti 398 nm line and the O 777 nm line measured during the sputtering of a Ti target in the metallic mode (upper graph) and in the oxide mode (lower graph) using a power of 1 kW, a frequency of 20 kHz, a reverse time of 10 µs, and a pressure of about 0.5 Pa.

3.1. Results of measurements during the ‘reverse time’

We chose the time at which the voltage to the magnetron is switched from the operating voltage to the reverse voltage (beginning of the ‘reverse time’) as the $t = 0$ point of our timescale. The voltage reversal takes a few tenths of a microsecond. The voltage reversal is accompanied by high-frequency oscillations in the MHz range, which were not clearly seen in all oscillograms. After about 1 µs, the voltage stays constant (and slightly positive) and the magnetron works as an anode. During the voltage reversal, the magnetron current changes its sign essentially as fast as
the voltage pulse from an ion current to an electron current due to electron bombardment of the cathode. No rapid oscillations in the current could be observed, which is most likely due to the fact that the current probe does not have a sufficient time resolution. The electron current declines slightly during the ‘reverse time’ as one would expect. The exact nature of the high-frequency voltage oscillations is not known. They may be a manifestation of plasma instabilities caused by electric field and electron temperature perturbations [25].

The plasma (electron) density decreases sharply during the first microsecond of the ‘off-time’ by about a factor of 5. Subsequently, the decay is more gradual with a time constant of probably more than 10 $\mu$s, similar to what was observed by Bradley et al [16], who reported a time constant of about 40 $\mu$s. The slow decay of the plasma density was difficult to quantify in our measurements due to the fact that our detection limit for the plasma density was about $2 \times 10^{15}$ m$^{-3}$. Since the typical ‘reverse time’ in most pulsed dc reactive magnetron sputter applications does not exceed about 10 $\mu$s, some ‘residual’ rarefied plasma always exists at the end of the ‘reverse time’ [9, 16, 17]. This, in fact, is not undesirable, as it facilitates the re-establishment of the plasma during the following ‘on-time’.

The two-step decay of the plasma density is attributed to the presence of two groups of plasma electrons in a magnetron plasma [26]–[31]. Earlier Langmuir probe measurements in pulsed dc magnetron plasmas showed the presence of a group of near-Maxwellian electrons with the electron temperature of about 0.5 eV (slow or bulk electrons) and a group of fast, beam-type, electrons with a highly non-Maxwellian energy distribution corresponding to an ‘effective electron temperature’ of about 4 eV. It is important, however, to keep in mind that the concept of an ‘electron temperature’ is an oversimplification in pulsed dc magnetron plasmas (even for the bulk electrons) and must be used with caution. The initial fast decay of the plasma density is attributed to the rapid disappearance of the fast beam electrons when the magnetron power is turned off, while the subsequent slow decay may be associated with ambipolar diffusion of electrons and ions to the grounded surfaces that surround the plasma.

The initial loss of the fast electrons in the beginning of the ‘reverse time’ was not detected in our time-resolved electron temperature measurements. This is most likely a consequence of primarily two factors. First of all, the plasma analysed by the Langmuir probe is significantly less dense than the plasma analysed optically. Secondly, the time resolution of the Langmuir probe measurements of up to 0.8 $\mu$s is of the order of the decay time of the fast electrons, which renders a reliable time-resolved measurement of their decay difficult. Bradley et al [16, 17] managed to observe the decay of the fast beam electrons in their time-resolved probe measurements and reported a subsequent decline of the electron temperature during the ‘reverse time’ from about 5 to 1.5 eV over a period of about 5 $\mu$s after the initial fast decay. Even though the low density of our plasma during the latter part of the ‘reverse time’ renders a reliable $T_e$ measurement difficult in the present study, the results of our probe measurements are not inconsistent with the findings reported by these authors. In the metallic mode, the plasma potential during the ‘on-time’ is a few volts positive relative to the grounded anode. This is common in cases where a large anode is used [32]. During the ‘reverse time’, the plasma potential is in the range 30–50 V, but generally slightly less positive than the 40–50 V applied to the magnetron. Thus, the plasma is not the most positive ‘electrode’. This situation is similar to what was observed previously in glow and magnetron discharges [29], where the surface area of the anode surface is much smaller than the surface area of the cathode. In our case, the magnetron is a grounded anode during the ‘off-time’ and the walls and substrate holder, which have a combined surface area that is 5 times larger than the magnetron surface area, serve as the cathode.
The rapid decay of the fast electrons at the beginning of the ‘reverse time’ is supported by the results of the time-resolved optical emission spectroscopic studies. As can be seen in figures 4 and 6, the decay of the Ar emission line at 750 nm has a fast initial drop followed by a much slower decline. For clarity of presentation and to facilitate an easy comparison of the decay times of the different emission lines, the emission intensities of the various emission lines were normalized to each other at the beginning of the ‘reverse time’. The Ar lines at 404 and 751 nm, which are not shown here, decay in a similar fashion. The initial fast decay of the Ar 750 nm line can be expressed by a single exponential decay with a time constant of $0.95 \pm 0.06 \mu$s. The main route to populating the emitting levels of these three lines is electron impact excitation of ground-state Ar atoms, which requires electrons with energies of more than 13 eV. Those energies are primarily found in the fast beam electrons, which disappear within a microsecond into the ‘reverse time’. Thus, the initial decay of the intensity of these emission lines is determined by the rapid disappearance of the fast beam electrons and can, in fact, be used to monitor the decay of the beam electrons in the afterglow as discussed in more detail in our earlier paper [23].

Careful inspection of the decay of the three initially fast-decaying Ar lines (750, 751 and 404 nm) throughout the entire 10 $\mu$s ‘off-time’ shows that these lines also decay with longer time
constants of about 3–5 $\mu$s or even longer at later times (which are difficult to determine accurately because of the low signal levels) after the rapid initial decay (figures 4 and 6). Since this decay time is much shorter than the decay time of the slow bulk electrons, we attribute the observed decay to the decline of the Ar metastable density. Thus, the emission intensity of these lines can be used to monitor the decay of the Ar metastable density (see also the discussion below).

The production of Al (or Ti) stops abruptly at the beginning of the ‘reverse time’. Nevertheless, Al (and Ti) emission lines are recorded during the entire duration of the ‘reverse time’. The 396 and 394 nm Al emission lines decay with a time constant of about 4 $\mu$s as seen in figures 4 and 6. In the case of the Ti emissions at 398, 399 and 400 nm, which were recorded with a better time resolution, the decay constant was about 4 $\mu$s. The initial fast decay of the Ti emission lines is again related to the rapid disappearance of fast electrons at the beginning of the ‘reverse time’. As the excitation of Al and Ti lines requires only a minimum electron energy of slightly more than 3 eV, the slow decay constants of both the Al and the Ti emissions are associated with a combination of two factors, the decrease of electron temperature of the slow bulk electrons and the decay in the density of Al and Ti atoms in the afterglow. The diffusion of Al and Ti atoms out of the viewing region of our optical detection system takes a few microseconds depending on the kinetic energy of the atoms, which can range from a few tenths of an eV to a few eV.

The Ar lines at 764 and 772 nm (which is not shown here) decay more slowly than the 750 nm line with time constants of about 4 $\mu$s, similar to the slow decay constant of the Al and Ti lines. The lower level of the Ar lines at 764 and 772 nm lines is metastable. The emitting levels of these lines can be excited directly from the Ar ground state, which requires electron energies that are only found in the fast beam electrons. This production route terminates quickly at the beginning of the ‘reverse time’. The levels can also be excited by electron impact from the Ar metastable levels, which requires only energies of $<3$ eV. However, the excitation of the Ar metastable levels from the Ar ground state by electron impact also requires comparatively high electron energies of at least about 12 eV and thus also terminates rapidly at the beginning of the ‘reverse time’. As discussed in detail earlier [23], a careful analysis of the processes populating the emitting level of the Ar 764 nm line during the ‘reverse time’ and of the temporal behaviour of the Ar metastable density during that time in terms of the pertinent cross-sections for excitation and ionization of Ar atoms in the ground state and in the metastable state yielded an estimate for the decay time of the Ar 764 nm intensity during the ‘reverse time’ that was comparable to the 4 $\mu$s measured decay time. Therefore, we correlate the decay of the Ar 764 and 772 nm lines to the decay of the Ar metastable density. Other processes contributing to the decay of the Ar metastable density may be collisions with Ti or Al atoms or electron excitation to higher-lying states. Super-elastic electron collisions are also possible, but we do not have enough data to ascertain the relevance of this process. However, we have established from our analysis that the decay of the Ar 764 and 772 nm lines can be used to monitor the decay of the metastable Ar atom density in the remote plasma.

The temporal behaviour of the plasma density and the electron temperature in the oxide mode is similar to that in the metallic mode with a rapid decrease at the beginning of the ‘reverse time’ and fast increase at the beginning of the ‘on-time’. Some minor differences during the ‘on-time’ will be discussed later.

The optical emission spectroscopic studies in the oxide mode focused on the same emission lines that were studied in the metallic mode, but also included the O 777 nm line, which is not present in the metallic mode. The Ar 750 and 764 nm lines as well as the Al and Ti lines exhibit
a temporal behaviour in the oxide mode that is similar to their behaviour in the metallic mode (figures 4 and 6). The O 777 nm line appears to decay in a fashion similar to the Ar 750 nm line. However, a detailed analysis shows that the decay of this line is rather complex and requires a double exponential fit yielding two decay times of about 1 and 4 \(\mu s\), respectively. The first decay constant is consistent with the approximately 1 \(\mu s\) decay constant obtained for the fast decaying Ar emission lines and can thus be attributed to the decay of the fast beam electrons in the plasma afterglow. The emitting O atoms can in principle be produced in a single-step dissociative excitation process from ground-state O\(_2\) molecules as well as via a two-step process, in which the O\(_2\) molecule is first dissociated by electron impact into two ground-state O atoms and the O atoms are subsequently excited in a second electron collision process. The first process requires a minimum electron energy of more than 16 \(eV\). The O\(_2\) neutral dissociation proceeds primarily through the A \(^3\Sigma_u^+\) and B \(^3\Sigma_u^-\) states which requires minimum energies of about 6 and 8.4 \(eV\), respectively [33]. The subsequent excitation of the O atoms requires more than 10 \(eV\). Thus, both pathways to the formation of excited O atoms require electrons of comparatively high energy and it is not surprising that the temporal decay of the O emission line initially follows that of the disappearance of the fast beam electrons. The second decay constant of about 4 \(\mu s\) is close to the decay constant obtained for the Ar 764 and 772 nm emission lines. Therefore, it is reasonable to attribute the slow decay of the oxygen line either to the decay of the Ar metastable density assuming, e.g., Penning excitation of oxygen by Ar metastables, or to O diffusion out of the viewing region of our optical detection system. We note that O atoms which are produced with significant access to kinetic energy in the O\(_2\) dissociation (more than 1.2 \(eV\)) have a residence time in the viewing area of our optical detection system that is comparable or even shorter than the observed 4 \(\mu s\) decay time. However, the bulk of the O atoms have access to kinetic energies below about 1.2 \(eV\) [34] and residence times ranging from about 6 to 20 \(\mu s\). It is difficult to assess quantitatively to what extent, if at all, these residence times impact on the measured decay time of the oxygen line.

### 3.2. Results of measurements during the ‘on-time’

The negative voltage pulse that is applied to the magnetron at the beginning of the ‘on-time’ shows a very narrow voltage overshoot followed by an oscillatory behaviour before stabilizing (figures 3 and 4). The oscillations have a much lower frequency than the oscillations observed at the beginning of the ‘reverse time’. The voltage overshoot is most likely caused by the pulsed power supply and was seen even when the deposition system was replaced in the circuit by a purely ohmic resistor. The current, which becomes an ion current, does not show an overshoot, but also shows some oscillations similar to the voltage oscillations. These voltage and current oscillations may be related to plasma instabilities.

The current at the beginning of the ‘on-time’ is a combination of a displacement current and conduction current. The displacement current is related to the formation of the plasma sheath as discussed below. The plasma sheath is formed in a few microseconds and the displacement current disappears. During the remainder of the ‘on-time’, the cathode current is determined by ion bombardment of the cathode and is essentially constant.

The plasma density increases rapidly at the beginning of the ‘on-time’ (figures 3 and 4). This rapid increase is followed by a much slower increase throughout the remainder of the ‘on-time’. The electron temperature increases sharply showing a very narrow peak of more than 15 \(eV\) with a temporal fwhm (full width at half maximum) of less than a microsecond that appears to mimic
the voltage overshoot [17] and then declines very gradually to a value in the range 4–5 eV. The initial increase in both the plasma density and the electron temperature and, especially the sharp peak in the electron temperature, are related to both the voltage overshoot and to the sheath formation.

The sheath formation proceeds in a few steps [35]. Since the plasma density does not go to zero at the end of the ‘reverse time’, there is a residual rarified plasma present at the beginning of the ‘on-time’. The electrons near the cathode are rapidly accelerated away from it by the electric field and an ion matrix sheath is formed. This occurs at a time that is determined by the electron plasma frequency, i.e. by the residual low plasma density at the end of the previous ‘reverse time’ and is of the order of a few nanoseconds to several tens of nanoseconds. The magnetic field of the magnetron redirects the accelerated electrons in a direction that is parallel to the surface of the target, which increases the time required for the formation of the matrix sheath. These accelerated electrons are most likely the reason for the observed spike in the electron temperature. Further development of the sheath involves a rearrangement of the ion density, which occurs on a timescale that is approximately five times the inverse ion plasma frequency [35], about a microsecond in the present case. Experiments show that the stabilization of the plasma in the vicinity of the substrate takes much longer by comparison. The reason for the slow plasma re-establishment near the substrate is not understood.

The plasma potential in the oxide mode is more negative by about 5–20 V than in the metallic mode and is negative with respect to the ground potential. This is most likely caused by the thin oxide layer that is eventually deposited on the anode and on the walls of the reaction chamber.

The temporal behaviour of the Ar 750, Ar 764, Al 396 and Ti 398 nm line emissions are very different when the plasma is re-established at the beginning of the ‘on-time’. The Ar 750 nm line rises rapidly and overshoots the steady-state level of the emission intensity, which is reached after about 10 µs. The Ar 764 nm line exhibits a much less pronounced overshoot and reaches its steady-state intensity level after about 5 µs. By contrast, the intensities of the Al and Ti lines increase much more slowly. There is no overshoot in the emission intensity and the lines do not reach their steady-state intensity level until more than 10 µs after the voltage pulse has been applied. This different behaviour of the lines can be understood on the basis of the temporal behaviour of the voltage and discharge current when the plasma is re-established (figure 4). The initial voltage overshoot produces a significant amount of energetic beam electrons, which in turn, leads to a significant population of the emitting level of the Ar 750 nm line during that period. Since the emitting level of the Ar 764 nm line is not as efficiently excited from the Ar ground state as that of the 750 nm line, the overshoot in the emission intensity of the 764 nm line is less pronounced. The gradual increase of the emission intensities of the Al 396 nm and Ti 398 nm lines, on the other hand, is due to the slowly increasing number density of Al and Ti atoms, which is largely determined by the slow increase of the discharge conduction current.

The temporal behaviour of the plasma density and the electron temperature during the ‘on-time’ show some minor differences in the oxide mode (with the Al target) compared to the metallic mode. While the respective decrease (at the beginning of the ‘reverse time’) and increase (at the beginning of the ‘on-time’) are similar, the plasma density during the ‘on-time’ in the oxide mode is higher than in metallic mode as is the average electron temperature. The higher plasma density is due to the higher cathode current. The cathode current in the oxide mode is also higher compared to the metallic mode (at the same power) due to the higher secondary electron emission from the oxidized target [36].
The optical emission spectroscopic studies in the oxide mode show results that are similar to those in the metallic mode. At the beginning of the ‘on-time’, the Ar 750 nm line recorded with Ti as a target has a narrow peak at the beginning of the ‘on-time’ that corresponds to the voltage overshoot (figure 6). By contrast, the O 777 nm line does not exhibit a pronounced overshoot. Subsequently, for a period of few microseconds, the optical emissions of all Ar lines and of the O line increase faster than the current. This indicates the important role of the fast beam electrons, whose density in the plasma decreases as the sheath is formed. Thus, the early part of the ‘on-time’ is more favourable for the generation of radicals than for sputtering.

4. Conclusions

We used time-resolved Langmuir probe measurements in conjunction with time-resolved optical emission spectroscopic studies to characterize the properties of pulsed dc magnetron plasmas. We show how a combination of time-resolved Langmuir probe measurements and time-resolved optical emission studies of pulsed dc magnetron plasmas can be used to extract more detailed information regarding the temporal variations of the critical plasma parameters and plasma species that can be obtained from only probe studies or from only optical measurements. The measurements were carried out using Al and Ti targets in Ar (metallic mode) or in Ar/O$_2$ (oxide mode). Cathode voltage and cathode current were recorded during the ‘reverse time’ and ‘on-time’ of the pulsed dc and correlated with data extracted from Langmuir probe studies (plasma potential, plasma density and electron temperature) and optical emission spectroscopic studies using several Ar lines as well as Al and Ti lines in the metallic mode or the O 777 nm line in the oxide mode.

When the plasma power is turned off at the beginning of the ‘reverse time’, the plasma density near the substrate decays initially very fast with a decay time of about 1 $\mu$s or less, which is attributed to the loss of the fast beam electrons in the plasma. This notion is supported by the initial decay of the Ar 750 nm line and the O 777 nm line, which have about the same decay constant. Subsequently, the plasma density and the intensity of all emission lines decay much more slowly with time constants around 4 $\mu$s. Since the bi-polar diffusion of the slow bulk electrons and the ions to the walls of the reaction chamber has a time constant in the range of a few tens of microseconds, other processes must be responsible for the 4 $\mu$s decay constants. Since the generation of Al and Ti atoms stops abruptly at the beginning of the ‘reverse time’, we attribute the observed 4 $\mu$s decay time to the diffusion of metastable Ar atoms and Al and Ti atoms in the metallic mode or O atoms in the oxide mode out of the viewing range of our optical detection system. In addition, Penning excitation of atomic oxygen by metastable Ar states and the electron-impact excitation out of metastable Ar states are likely to occur. Penning excitation of Al and Ti by Ar metastable states cannot be excluded, even though the energy difference is comparatively large, which renders it as a rather inefficient process.

When the negative voltage is abruptly turned on at the beginning of the ‘on-time’, a pronounced voltage overshoot is observed accompanied by a rapid increase in the plasma density in a fraction of a microsecond and a narrow peak in the electron temperature. Subsequently, the plasma density increases more slowly during plasma re-establishment and the formation of the sheath, which requires a few microseconds depending to a large extent on the residual density of the rarefied plasma that is still present at the end of the ‘reverse time’. The intensities of the Ar and O lines show a more or less pronounced overshoot at the beginning of the ‘on-time’, which
is not found in the cathode current and the plasma density. By contrast, the emission intensities of Al and Ti lines follow the rise in the discharge conduction current.

Acknowledgments

This work was supported in part by the US National Science Foundation (NSF), by the US Army TACOM/ARDEC under contract DAAE30-00-D-1011 DO#20-1 (Picatinny Arsenal), and by Advanced Energy Industries, Inc. Partial financial support of this work by the NSF through an AGEP grant to JL is also gratefully acknowledged. JL was also a recipient of a MAC Doctoral Fellowship from the State of New Jersey.

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