Transport of ionized metal atoms in high-power pulsed magnetron discharges assisted by inductively coupled plasma

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Transporting metallic ions from the magnetron cathode to the substrate is essential for an efficient thin-film deposition process. This letter examines how inductively coupled plasma superimposed onto a high-power pulsed magnetron discharge can influence the mobility of titanium ions. To this effect, time-resolved optical emission and absorption spectrometry are conducted and the current at the substrate is measured. With this new hybrid technique, ions are found to reach the substrate in two successive waves. Metal ions, only present in the second wave, are found to accelerate proportionally to the power supplied to the inductively coupled plasma. All the measurements in this study are made at 10 and 30 mTorr, with 10 μs long pulses at the magnetron cathode. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2162671]

High-power pulsed magnetron sputtering is an emerging ionized physical vapor deposition (IPVD) process. This technology offers the possibility to deliver very high peak power pulses to the discharge gas (hundreds of kilowatts) in order to produce ionized metallic vapor,[1] the average power delivered to the cathode remaining in the range of conventional magnetron discharges. This allows the coating synthesis to be better controlled and the film properties (adherence, wear resistance, compactness, etc.) to be improved.[2,3] As a consequence, the field of application of magnetron sputtering technology is broadening. However, there is a major drawback: its deposition rate is low compared to those of conventional magnetron technologies.[4] With this kind of IPVD process, most of the metal atoms sputtered away from the cathode are ionized in the dense magnetron plasma created by the highly negative pulsed voltage (a few kilovolts). Transporting metal ions to the substrate holder is not simple; however, efficient transport and collection of the metal ions could minimize the decrease in deposition rate. The first key aspect is to balance the ions' electrical space charge as they cross the cathode-substrate space,[5] where the medium has to be electron rich. In addition, as the metal ions leave the region near the cathode, they have to be replaced by background gas ions in order to ensure space charge neutralization of the magnetized plasma. Both criteria can be fulfilled by creating a secondary plasma between the cathode and the substrate holder. Therefore, the density of this plasma is a critical characteristic of the system. In this study, we have chosen to improve the ion transport by adding a secondary inductively coupled plasma (ICP) and to examine the influence of the power supplied to the ICP on the mobility of the metal ions.

The experimental setup used was previously described in Refs. 6 and 7. The only difference is that a high-power pulse generator replaces the magnetron dc power supply.[8,9] This particular power supply is especially designed to produce pulses of short duration (<20 μs). Figure 1 represents the current and voltage evolution of the pulse applied to the circular titanium magnetron target (10 cm in diameter) at a pressure of 10 mTorr (1.4 Pa). The breakdown delay of the discharge current is short, and, taking into account the race-track surface, the magnetron current density peaks at $\sim 1-2$ A/cm^2. The copper coil for ICP plasma generation is located 4 cm above the magnetron cathode, halfway between the target surface and the substrate. The ICP is powered by a 13.56 MHz rf generator. The circular substrate holder (8 cm in diameter) can be electrically insulated from the ground or dc negatively biased to repel the high-energy electrons produced during the discharge pulse. At 10 mTorr, a bias voltage of -40 V is the minimum value necessary for that pur-

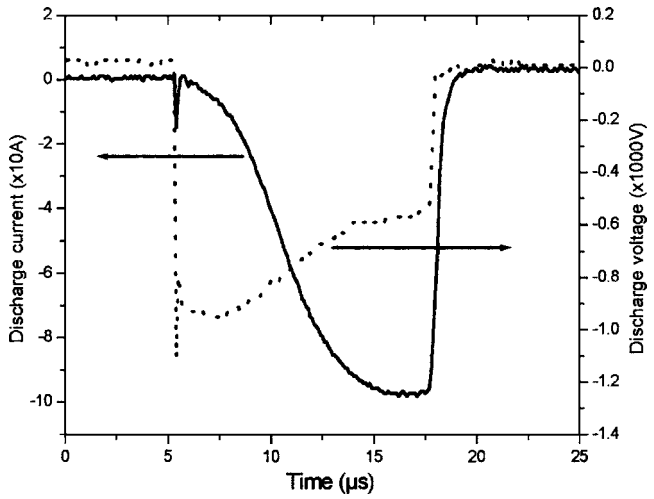

FIG. 1. Current and voltage characteristics of a 12 μs long pulse at a pressure of 10 mTorr (1.4 Pa). Pulse frequency is 760 Hz.

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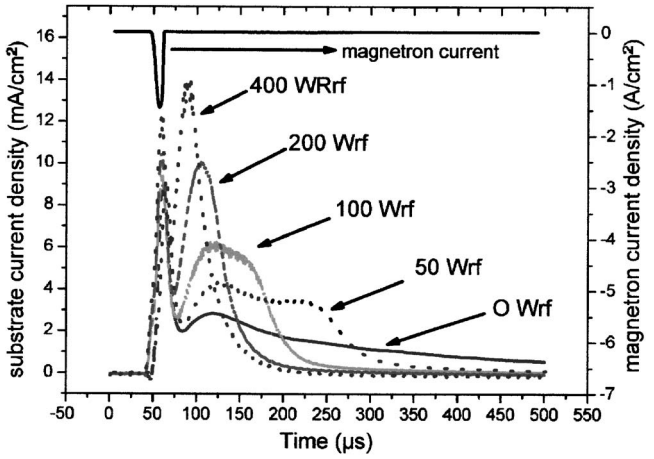

FIG. 2. Time-resolved substrate current density at 10 mTorr for different rf powers applied to the coil. The substrate holder is biased to −40 V.

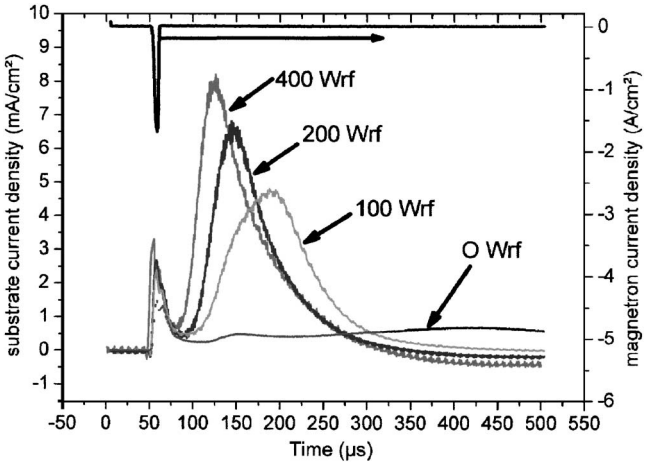

FIG. 3. Time resolved substrate current density at 30 mTorr for different rf powers applied to the coil. The substrate holder is biased to −40 V.

pose. At a higher pressure of 30 mTorr, the bias voltage needed is lower due to the higher collision probability for electrons in the gas. All the experiments are conducted in pure argon gas and using a bias voltage of −40 V. The measurement of the electric current drawn by the substrate holder is time resolved, as is the Ti^+ optical emission intensity. For the optical measurements, the Ti^+ line at 368.5 nm is chosen. Thanks to the titanium pulsed hollow cathode lamp (HCL) described in Ref. 7, it is possible to implement time-resolved atomic absorption spectroscopy (AAS) to detect Ti^+ ions. Both emission and absorption spectroscopic tools are placed 5 cm above the magnetron target, between the rf coil and the substrate holder. The magnetic field has a value of $\sim 2 \times 10^{-3}$ T at this position. The same optical fiber that is used to collect the light emitted by the HCL and that produced by the magnetron plasma is protected by a cylindrical collimator array whose total diameter is 1.5 cm. The latter is composed of smaller tubes ~1 mm wide and 2 cm long. The quartz window allowing the HCL light to enter the vacuum chamber and to cross its diameter (25 cm) is placed in front of the optical fiber. With this geometry, excited atoms produced in the plasma (emission spectroscopy) and traveling across the gap between the target and the substrate can be detected. In cases where Ti^+ ions are not excited, they can be detected using the AAS. All the signals are recorded using a digitizing oscilloscope (Tektronix TD420A).

Figures 2 and 3 report the time evolutions of the substrate and magnetron current densities at 10 and 30 mTorr, respectively. The left-hand scale corresponds to the substrate current density, the right-hand scale, to the magnetron current density. The peak voltage is set at 1.1 kV and the discharge pulse is 10 μs long. Observing both figures, one can see that the ions settle onto the substrate surface in two waves, whether the coil is powered or not. The first wave reaches the substrate only a few microseconds after the electrical pulse is initiated. Therefore, those ions are very fast. Their speed, estimated as the time elapsed between the maximum of the first wave and the discharge current maximum divided by the target-to-substrate distance (8 cm), is in the range of 10^4 m/s. The temporal position of this first wave is not influenced by the rf secondary plasma. There are two possible reasons for this behavior. Firstly, the plasma generated by the rf coil is not as dense as the pulsed plasma. For the magnetized plasma near the cathode, the electron density can be roughly estimated using the magnetron current density (~ 2 A/cm^2) and the Child-Langmuir law. A value of $\sim 10^{14}$ cm^{-3} is found. For the plasma developed in the target-to-substrate gap, in similar conditions, Gudmundsson *et al.*[10] experimentally measured an electron density around 10^{12} cm^{-3} using a Langmuir probe. This last value is one order of magnitude greater than that obtained with the rf coil using an rf-compensated Langmuir probe (SmartProbe, Scientific Systems Ltd). Secondly, the increase in gas temperature induced by the rf [up to 500 K with 500 Wrf (see Ref. 11)] and the associated decrease in local density are certainly weak compared to the gas heating produced by the sputtering wind generated by the 100 A magnetron pulse current.[12] In other words, the plasma, during the pulse, seems to be governed by the pulsed discharge.

Macàk *et al.*[13] postulated that the first ions reaching the substrate are Ar^+. Those ions are produced at the early stages of the pulse due to the ionization front generated by the fast electron beam crossing the target-to-substrate gap. To identify the composition of the first wave, time-resolved AAS measurements were made. As presented in Fig. 4, at

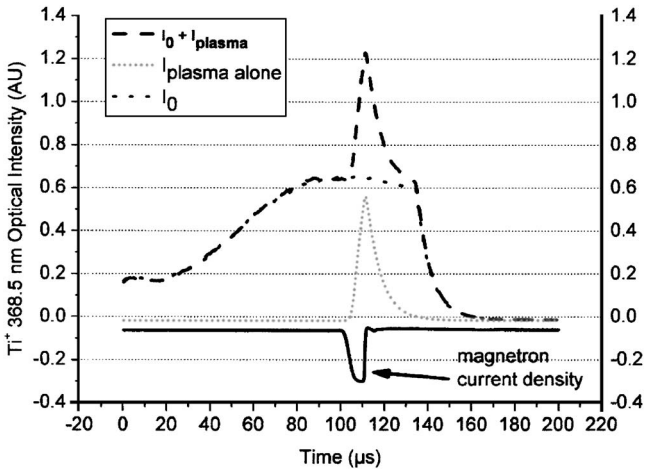

FIG. 4. Time-resolved AAS on Ti^+ at 30 mTorr. $I_{o+plasma}$ signal is the arithmetical summation of the line intensities emitted by the magnetron discharge (I_{plasma}) and the HCL (I_o), proving the absence of Ti^+ in the cathode-to-substrate gap during pulse and up to 30 μs after the discharge current peak. Magnetron current density curve (not drawn to scale) is used as a temporal reference.

30 mTorr, the Ti^+ line intensity (I_{plasma}) coming from the magnetron adds up arithmetically to the HCL signal (I_0) to give the intensity labeled $I_{0+plasma}$. Therefore, no metal ions are detected, the absorption coefficient, defined as $A=1-[(I_{0+plasma}-I_{plasma})/I_0]$, being negligible. Our results confirm that Ar^+ should be the only ions composing this first wave.

The second wave is attributed to ions slowly diffusing during the postdischarge regime. The shape of this part of the curves and the temporal position of their maximum are a function of the gas pressure (compare Figs. 2 and 3). At higher pressure, the curve is flattened, so that the ions obviously travel slowly at high pressure. This time delay could have two possible explanations. Firstly, the electron density in the interelectrode space is weak, causing the compensation of cationic charges to no longer be efficient and therefore dramatically decreasing the efficiency of the transport. Secondly, the gas has had enough time to cool down, making the collision frequency greater than during the pulse. Figures 2 and 3 show the effect of the rf coil on the acceleration of the ions belonging to this wave. As the rf power increases, ions from the second wave are collected more and more rapidly. One can notice, for 10 mTorr, 50 and 100 Wrf, that the second wave presents a plateau region. In these conditions, plasma density near the substrate is not significant enough to allow efficient transport and collection of the ions. The acceleration produced by the rf coil is greater at 30 mTorr because at that pressure, the coupling between the plasma and the coil is more efficient. The electron density (n_e), as measured by an rf-compensated Langmuir probe (SmartProbe, Scientific Systems, Ltd.), is higher due to the increased collision rate: $n_e \sim 10^{11}$ cm^{-3}, 1 cm above the coil plane at 30 mTorr, while $n_e \sim 10^{10}$ cm^{-3} at 5 mTorr.[14] A rise in gas temperature[11] should also play a role in transporting the ions: when the rf power is on, the interelectrode gas becomes more conductive. As a result, at 10 mTorr, the ions (already traveling at a high speed without rf power) are accelerated by a factor of 2: up to ~2300 m/s with 400 Wrf. At 30 mTorr, they are accelerated more significantly, from 220 m/s with 0 Wrf up to 1140 m/s with 400 Wrf.

Concerning the ionic composition of the postdischarge, Ti^+ emission appears for the second wave only if the ICP is superimposed onto the pulsed discharge, as presented in Fig. 5 for a 10 mTorr pressure, with 0 and 400 Wrf. Without inductive plasma, there are no electrons to allow a significant excitation of the Ti^+. The luminous signal behaves with the rf power in a similar way as it does to the substrate current, confirming that the second wave carries titanium ions. In addition, time-resolved AAS measurements made at 10 mTorr, 0 Wrf, and 150 μs after the pulse showed a strong absorption of Ti^+ ions ($A \sim 50\%$). To estimate the total charge density impinging on the substrate surface, all the substrate current curves presented in Figs. 2 and 3 have been wholly integrated. It is found that the rf plasma does not strongly modify the amount of ions reaching the substrate: the quantity of ions created using rf power is insignificant compared to that produced using the high-power pulsed magnetron. At 10 mTorr, the calculation yields a value of 800 ± 40 nC/cm^2. At 30 mTorr, the integration results in a smaller value of 600 ± 35 nC/cm^2 (without taking into account the 0 Wrf curve) due to the broad scattering of the sputtered particles. The area corresponding to 30 mTorr, 0 Wrf, is smaller than the areas obtained at 30 mTorr with the ICP turned on. This is due to the fact that the whole current curve associated with this condition is not completely taken into account for the integration calculations: the tail of the curve is missing because the ions are extremely slow (see Fig. 3). The curve maximum appears at approximately ~450 μs.

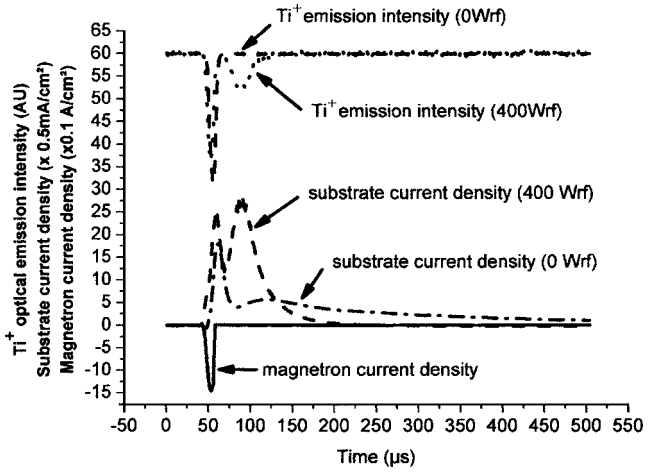

FIG. 5. Comparison between the time evolution of Ti^+ optical intensity, and magnetron and substrate current densities at 10 mTorr, for 0 and 400 Wrf.

In conclusion, it is shown that using a hybrid process composed of an ICP superimposed onto a high-power pulsed sputtering discharge causes an accelerated collection of ions by the substrate. This effect could minimize the decrease in the deposition rate due to self-sputtering and redeposition, as the metallic ions are not able to leave the magnetized plasma because of the lack of electrons in the space between the target and the substrate. Finally, thanks to the secondary plasma, time-resolved optical emission measurements have been made to analyze the postdischarge and to bring to light the fact that metal ions belong to the second wave that reaches the substrate.

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