Dynamic of film growth during high power pulsed magnetron sputtering (HIPIMS) of titanium

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Abstract: The plasma dynamic of HiPIMS is followed by optical emission spectroscopy, time and energy resolved ion mass spectrometry with a resolution of up to 1 µs. The different contribution to the ion energy distribution in energy and time are resolved.

Keywords: high impulse power magnetron sputtering, ion energy mass spectrometry

1. Introduction
HiPIMS plasmas are magnetron discharges, which are operated in a pulsed mode with peak powers in the range of several kW/cm$^2$ and duty cycles in the range of a few percent or less. Based on this pulsing technique, the plasma density and ionization degree in the pulse can be very high while limiting the thermal load on the substrate.

A HiPIMS pulse follows a sequence of 5 phases [1]: (i) a voltage is applied to the target and the plasma is ignited. During the very first microseconds, the plasma potential in front of the target becomes very negative of the order of -200 V [2,3] causing strong electric fields are created. All ions are trapped and only those with very high energies or those that are created outside of the magnetic trap are able to reach the substrate. The gas temperature increases to 1200 K; (ii) in phase2 (current rise), the current increases due to a plasma bulk breakdown sustained by secondary electrons. A dense plasma torus is developing above the racetrack of the target. The voltage drop is most pronounced only in the sheath region in front of the target; (iii) (gas depletion), the emission of neutrals and ions of the sputtered material become visible. At these conditions, the working gas neutral density decreases due to ionization and due to gas rarefaction driven by the hot plasma; (iv) in phase 4 (plateau/runaway), a steady state is reached with a target current depending on working gas and target material as well as on the self-sputtering coefficient; (v) in phase 5 (afterglow), the electron density decays following two time constants, a fast decay of the order of 30 µs followed by a much slower decay of the order of 3 ms [4]. The electron temperature rapidly decreases.

The incident ion fluxes on the substrate have been measured by several groups using time-integrated and time-resolved ion mass spectrometry either monitoring at substrate level in direct line-of-sight to the magnetron target or sideways at the target level. The temporal resolution is often only 20 µs [4], which makes it difficult to resolve the HiPIMS pulses with typical pulse lengths of 70 µs to 200 µs. Therefore, only time-averaged data or the time-dependent decay in the afterglow with decay times of the order of ms are discussed.

In this paper we follow the dynamic of a HiPIMS pulse by combining three techniques, phase resolved optical emission spectroscopy (PROES), time- and energy-resolved ion mass spectrometry (MS), and time-resolved measurement of the film growth using a rotating shutter experiment [6,7]. As a result, we seek to connect the time-resolved growth rate with the temporal evolution of the energy- and mass-resolved incident ion flux.

2. Experiment
The experiments are performed in a vacuum vessel housing a 2 inch magnetron with titanium target, which is powered by a Melec HIPIMS power supply (see Fig. 1) producing rectangular voltage pulses. The substrate consists of a silicon wafer, which is inserted into a 6-inch substrate holder using a load lock system. Argon gas is used as plasma forming gas at a pressure between 0.25 Pa and 1 Pa. A HIPIMS pulse length between 50 µs and 400 µs is used at different duty cycles. The average power is adjusted to between $\langle P \rangle > 60$ W and $\langle P \rangle < 100$ W. Current and voltage at the target are monitored with a voltage-current (VI) probe. During current maximum after 40 µs, a specific peak power $P_{peak}$ is dissipated before the HiPIMS plasma reaches a plateau phase with a lower power of $P_{plateau}$.

Time- and energy-resolved ion mass spectra are measured using a HIDEN EQP 300 instrument, which is mounted in line-of-sight to the racetrack of the magnetron target, as shown in Fig. 1. The mass spectrometer is mounted in a differential pumping stage with a base pressure of $10^{-8}$ mbar and a sampling orifice of 100 µm.
The EQP provides a time-resolved measurement mode based on the boxcar method with a temporal resolution of only 20 µs, which is rather poor to resolve the dynamic of HiPIMS pulses with lengths between 50 µs and 400 µs. To overcome the limited time resolution, we employed a multi channel scaler (MCS) to store the signal from the secondary electron multiplier of the EQP in sync with the HiPIMS pulsing. Thereby, the temporal resolution is only limited by the sampling rate of the MCS which is of the order of 32 ns. To acquire sufficient signal intensity, we set the measurement window in the MCS to 1 µs, and collected at a given mass and energy the temporal evolution of the signal. The energy is scanned in steps of 0.25 eV for energies between 0 eV and 20 eV. These data correspond to a map of signal intensity versus time and energy. By integrating over all energies, a time resolved total ion current is obtained.

The discussion of time-resolved data relies on an exact synchronization of the signals from the VI probe, the ICCD camera, the EQP and the rotating shutter experiment. By adjusting the time scale for all data using the distinct features at the end of the HiPIMS pulse, we define this time scale with respect to the measurement orifice of the EQP at the substrate position. By using this approach, we also automatically correct for the different time-of-flights (TOF) of the ions in the mass spectrometer.

3. Results and Discussion

The temporal evolution of the ion fluxes are plotted for a 200 µs HiPIMS pulse at a pressure of 0.25 Pa, 0.5 Pa and 1 Pa in Fig. 2. The following conclusions can be drawn:

- **Initial peak in the argon ion current:** Due to the excellent temporal resolution, we may also identify a pronounced peak in the argon ion flux at the very beginning of the HiPIMS pulse. This is consistent with the traveling ionization zone as being observed phase resolved optical emission (not shown). We assume that the ionization zone may also generate argon ions locally in front of the substrate, which are then observed as a peak in ion current, when the ionization zone arrives at the substrate 25 µs after plasma ignition (marked as 1 in Fig. 2). This initial pronounced peak...
is absent in the titanium ion spectra. This is consistent, since the titanium neutral density in front of the substrate directly after the onset of the HiPIMS pulse is still small.

- **Delay between argon ions and titanium ions:** Argon ions are observed earlier than titanium ions. This is consistent with findings in the literature [5], where it is explained by the fact that the sputtering requires some time to build up before titanium ions become visible.

- **Peaks of ion current in the late afterglow:** A peak in the ion current is observed after the end of the HiPIMS pulse (marked as 2 in Fig. 2). This peak is very pronounced at higher pressures as can be seen in Fig. 2c. The explanation of the ion current peak in the afterglow on the dynamic of plasma generation in HiPIMS: during the on-time of the pulse, an intense ion population is confined in the magnetic trap in front of the target. The transport time from target to substrate for these ions can be much larger than the transport time of neutrals due to the larger cross sections for ion-neutral collisions compared to neutral-neutral collisions. The arrival time at the substrate position is later for higher pressures, due to the collisional nature of the transport, as can be seen by the shift of the position of the ion peak (marked as 2 in Fig. 2).

- **Sharp increase in the ion current at plasma shut off:** In several experiments (marked as 3 in Fig 2a), a peak in ion current is observed directly after switch off of the plasma. The inspection of the ion energies, as shown below, reveals that directly after the plasma shut off, the energy *increases* typically for 10 μs. This can be explained by a short increase of the plasma potential directly after switch off of the plasma, as also observed by the emissive probe measurements by Mishra et al. [2,3]. Due to this fast change in plasma potential, the sheath in front of the substrate quickly expands into the plasma bulk in front of the substrate. Suddenly, the ions in front of the substrate experience an electric field of the expanding sheath and are accelerated towards the substrate.

- **Ion fluxes during the plateau phase of the pulse:** As discussed before, the travel time of the ion population from magnetron target to substrate may be rather long. Nevertheless, we see a constant argon and titanium ion flux towards the substrate, which follows the plasma current. We assume that these ions can only be created from ionization of argon or titanium neutrals directly in front of the substrate. If titanium is sputtered at the target it is emitted as neutral species with a Thompson energy distribution. If these species remain neutral, their free mean path is large and they may reach the substrate within a 50 μs. This makes them much faster than the trapped ion population which has to travel across the magnetic field lines within 250 μs from target to substrate. Due to the ionization of the fast neutrals in front of the substrate, the ion current depends rather directly on the plasma current, which ex-

![Fig. 3 Contour plot of the ion current for a HiPIMPS pulse at 200 μs and 0.25 Pa for Ti²⁺ (a) and Ti⁺ (b); (c) energy distributions for Ti⁺ at 60 μs (open circles), at 100 μs (solid circles), and at 220 μs (open squares). Energy distribution according to a shifted Maxwellian for T_i = 0.85 eV an E_shift=4.3 (eV) (dashed line), for T_i = 0.15 eV and E_shift=1.3 (eV) (dotted line), and according to a Thompson distribution for E_shift=4.9 (eV) (dashed dotted line).]
The dynamic of the incident ion currents in a HiPIMS plasma is analyzed in more detail by regarding the temporal evolution of the energy distributions for a pulse length of 200 µs and a pressure of 0.25 Pa. The time dependent energy spectra are shown as contour plots for Ti^{2+} in Fig. 3a and for Ti^{+} in Fig. 3b, respectively. The energy distributions are plotted at 60 µs, 100 µs, and 220 µs in Fig. 3c together with a Thompson distribution function for a surface binding energy of $E_{\text{sbe}} = 4.9$ eV and a Maxwellian distribution shifted by $E_{\text{shift}}$ with an ion temperature of $T_{\text{i,kin}}$.

- **at 60 µs, current maximum:** during the current maximum between 40 µs to 60 µs the plasma is most intense, inducing a high flux of sputtered titanium, which eventually becomes ionized on its transport to the substrate. The energy distribution of Ti^{+} can be very well fitted by a shifted Maxwellian with an energy shift of $E_{\text{shift}} = 4.3$ eV and an ion temperature of $T_{\text{i}} = 0.85$ eV. This is consistent with the transport of neutrals followed by their ionization in the plasma and thermalization by ion-ion collisions.

- **at 100 µs, plateau phase:** the HiPIMS plasma is in its plateau with a moderate current and a locally reduced density due to gas rarefaction. Fig. 3c shows that the energy distribution can be best fitted by the sum of shifted Maxwellian with an energy shift of $E_{\text{shift}} = 1.3$ eV and an ion temperature of $T_{\text{i}} = 0.15$ eV and a Thompson distribution to account for the high energy tail of the distribution. Such a bimodal distribution seems reasonable, because the plasma density drops in the plateau phase so that any thermalization of the ions is reduced.

- **at 210 µs, after plasma shut off:** directly after plasma shut off, the ion energies increase by 1 eV as illustrated in Fig. 3a, b. As introduced above, the loss of hot electrons after plasma shut off causes the plasma potential to rise for a few µs, inducing the burst of energetic ions, which was already seen in Fig. 2.

- **at 220 µs, afterglow:** In the late afterglow the ion energies are very small, indicating a very low electron temperature in the decaying plasma. The distributions can be well described by a shifted Maxwellian with energies $E_{\text{shift}}$ and ion temperature $T_{\text{i}}$ of the order of a few 0.1 eV.

Summarizing we can state that the temporal evolution of the incident ion fluxes follows a very complex sequence: after a first initial burst of argon ions, the ion flux is dominated during the on time of the pulse by incident ions, which originate from ionized neutrals in front of the substrate. Due to the long transport time from target to substrate, an ion population from the magnetic trap in front of the target reaches the substrate very later, which is eventually after the end of the HiPIMS pulse.

### 4. Conclusion

The temporal distribution of the incident fluxes of ions on the substrate during a HiPIMS pulse with pulse lengths between 50 µs to 400 µs and peak powers up to 6 kW by energy resolved ion mass spectrometry. Four ion contributions impinging on the substrate at different times and energies are identified:

(i) after ignition, an ionization zone travels to the substrate and ionizes argon neutrals in front of the substrate leading to an initial argon ion burst at 30 µs after ignition, (ii) during the current maximum at 50 µs an ion population is created in front of the target, which reaches the substrate only after few 100 µs depending on pressure. (iii) during the on time of the HiPIMS pulse, the ion current on the substrate is dominated by argon and titanium ions originating from ionized neutrals in front of the substrate. (iv) at plasma shut down, a small spike of ions is observed, when the ion density in front of the substrate is high. This burst of ions is induced by a change in plasma potential due to the loss of hot electrons.

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### 5. References