Semion retarding field energy analyzer used to investigate reactive HiPIMS + MF sputtering of TiO₂ crystalline thin films*

**STUDY**

Hailed as an advantage, high-power impulse magnetron sputtering (HiPIMS) systems have been previously studied with mid-frequency (MF) plasma excitation, utilizing the “off” period to enhance the deposition rate, decrease the working pressure, and improve HiPIMS plasma generation. This study measured the time-resolved ion velocity distribution function (IVDF) in a high-power pulse plasma in three modes of excitation: pure HiPIMS, medium-frequency pulsed bipolar (MF 350 kHz) and hybrid pulsed HiPIMS + MF.

Three types of atmospheres were used in the study: inert pure Ar, a reactive mixture of Ar + O₂, and a reactive mixture of Ar + O₂ + N₂. The gas pressure was kept constant at p = 1 Pa.

**METHOD**

The experiment was set up as follows:

A Semion retarding field energy analyzer (RFEA) was placed at the substrate position 80mm below the target to measure the ion velocity distribution function (IVDF). The Semion consists of a series of grids behind the sampling apertures and is terminated by a collector plate, as illustrated below:

**Figure 1:** Experimental setup of the hybrid DC pulsed HiPIMS + MF magnetron sputtering system for low- and high-pressure sputtering.

**Figure 2:** Schematic setup of the RFEA structure.
The Semion was positioned so that the entering apertures faced upstream. The orifices measured 800µm in diameter and allowed ions enter the RFEA for analysis. Under a series of assumptions, the ion velocity distribution, \( f(v) \), was calculated from the first derivative of the current-voltage characteristic using the following equation:

\[
f(v) = -\frac{m}{e^2} \frac{1}{\bar{P} \bar{A}} \frac{dI_c}{d\Phi}
\]

In this equation, \( m \) represents the mass of ions, \( \bar{P} \) is the total geometrical transparency of the grids, \( \bar{A} \) is the open area of the entrance orifice, \( e \) denotes elementary charge, \( I_c \) is collector current, and \( \Phi \) is the discriminator voltage. In our case, the measured \( I_c \) is the total sum of all ion contributions.

The four graphs below depict the typical discharge voltage and current waveforms for both pure HiPIMS and hybrid HiPIMS + MF magnetron during selected experiments:

A  A pure HiPIMS in an Ar atmosphere
B  HiPIMS + MF (350 kHz) in an Ar atmosphere
C  Pure HiPIMS in a reactive Ar + O\(_2\) atmosphere
D  HiPIMS + MF in an Ar + O\(_2\) atmosphere
**FINDINGS:**

The first graph below illustrates the time-resolved, normalised total ion flux on the substrate for various plasma conditions. Although there is no significant shift between the HiPIMS and HiPIMS + MF signals in an inert Ar atmosphere, in a reactive atmosphere, the difference between the two is consistently about 20 µs.

The next graph below shows time-averaged IVDFs for various gas mixtures and excitation modes. There are two findings from this graph: ion energy is the highest for an inert Ar plasma, and in a reactive plasma, the IVDF maximum is shifted upward by about 5 eV for HiPIMS + MF excitation relative to pure HiPIMS magnetron.

All TiO\(_2\) thin films deposited in reactive atmospheres formed pure rutile phase in every one of the excitation modes. However, films deposited by the HiPIMS + MF excitation mode demonstrated the greatest ability to produce a photocurrent.
HiPIMS + MF excitation in a reactive atmosphere was also found to effectively reduce the delay between the edge of cathode voltage and current onset. In addition, HiPIMS + MF was found to be best for the deposition of crystalline TiO$_2$ on polycarbonate foil thanks to the low heating flux on the substrate and suitable plasma parameters leading to the formation of the rutile phase.

**USES OF THE STUDY:**

These findings were especially significant for pulse plasma formation in the presence of reactive gases, as the delay between current pulse and applied voltage was about 20 μs faster for HiPIMS + MF than for pure HiPIMS.