Investigation of HIPIMS in a reactive atmosphere discharge with Oxygen content by energy resolved mass spectrometry

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Introduction

High power impulse magnetron sputtering (HIPIMS) is a new method for physical vapour deposition (PVD) based on magnetron sputtering [1,2]. It utilises transient impulse (short pulse) glow discharges with very high power and current density (up to 3 kWcm^{-2} and 4 Acm^{-2} respectively at a duty cycle of <5%). Under these conditions the plasma density near the target increases sufficiently to ionise a significant proportion of the sputtered metal ions [2,3] thus creating a high-efficiency metal ion source. Due to a low duty cycle, a high power density is applied at the cathode yielding a higher degree of plasma ionization than in conventional magnetron sputtering. Recently, HIPIMS has been used for deposition of oxides in particular for TiO_2 and TiO_xN_y.

In this study, the operation of HIPIMS in an Ar and variable concentrations of air with a Ti target was investigated. Plasma was operated at a pressure of 1-1.7 Pa and a Ar:Air partial pressure ratio ranging from 45:1 to 45:10 was used to operate at the metallic to poisoned transition point. The peak current was varied from 3 to 10 A with a pulse duration of 200 µs. The frequency was adjusted between 100 and 400 Hz to maintain a constant average power of 0.6 kW.

Mass spectrometry measurements showed that the reactive HIPIMS discharge produced a deposition flux with a significantly increased content of ionised film-forming species, such as Ti^{1+}, Ti^{2+}, N^{1+}, O^{1+}, TiO^{1+} and TiO_2^{1+}. Increasing the air content in the discharge resulted in an enhanced activation of the oxide species, TiO^{1+} and TiO_2^{1+}, and a reduction in the atomic ion N^{1+}, Ti^{1+} and Ti^{2+}. Ions with energies up to 80 eV were detected during the pulse with reducing energy in the pulse-off times in the metallic mode. The ion energy decreased considerably when the discharge was operated in the oxide mode.

In the mass spectrum of the negative ions only the O^- and O_2^- species were observed .The detailed study of the energy distribution of O^- and O_2^- shows high-energy ions formed at the cathode with energies proportional to the full cathode voltage. The ion energy distribution function shows that in the transition from metallic to the oxide mode there is about 100 V drop of the voltage on the oxide surface layer on the cathode; this corresponds well with the measured cathode voltage.

The effects of the oxygen content in the deposition flux observed in the HIPIMS discharge on the film microstructure are discussed.

Experiment

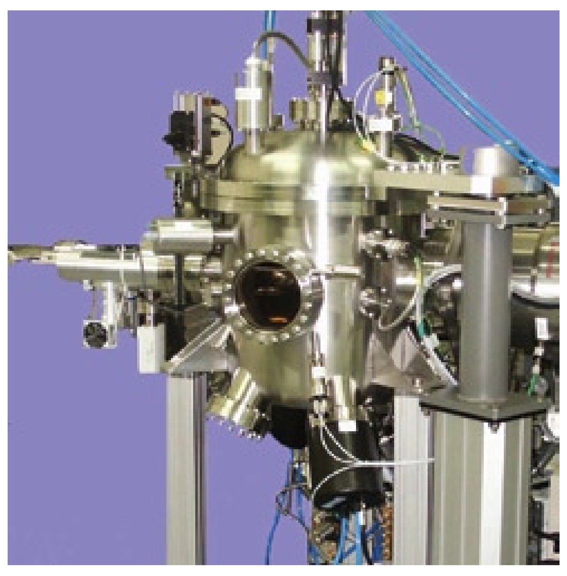
Equipment:

- Ultra high vacuum (UHV) chamber, base pressure of < 10^{-9} mbar
- One magnetron (Torus™, Kurt J Lesker) diameter of ø75 mm Ti target
- HIPIMS Power Supply from Hüttinger Electronic Sp.z o.o. Poland

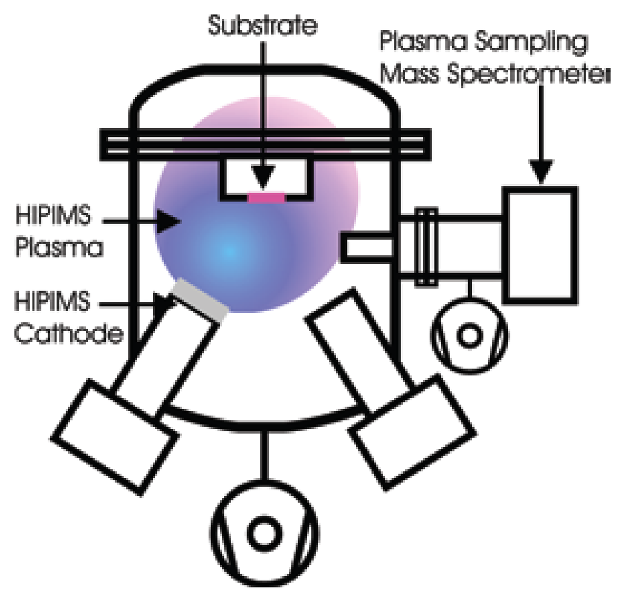
Energy-resolved mass spectroscopy at substrate position:

- EQP-HE-300, Hiden Analytical Ltd
- Distance to target = 50 mm
- Plasma sampled through a ø100 µm grounded orifice, acceptance angle of 5º
- Ion collection gated with a TTL output from power supply
- Measure a 70 µs window centred at the peak of the 150 µs pulse

Photo of UHV Chamber – Kurt J Lesker, Ltd.



Schematic Cross-section of UHV Chamber



HIPIMS

- **Identical average power** = 600 W
- **HIPIMS Discharge**:

Peak current (A) 3-10
Pulse frequency (Hz) 100-400
Pulse duration of 200 *µs*

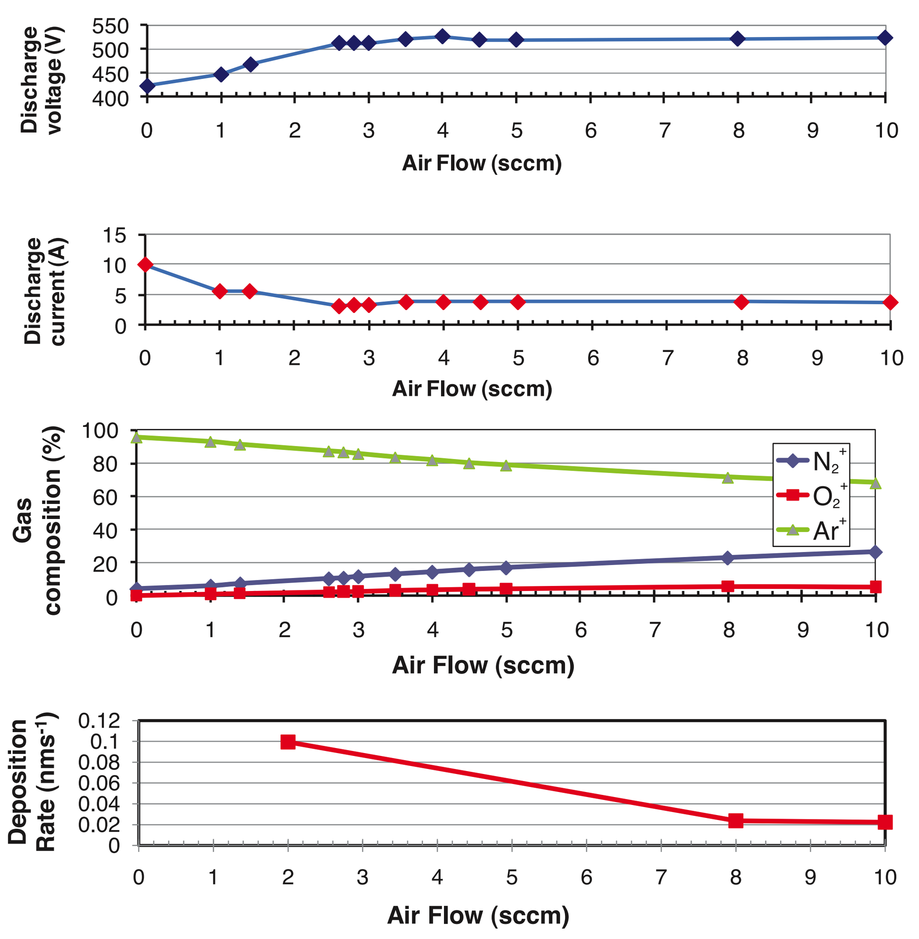
- **Reactive atmosphere**: Ar + Air

Total Pressure = 1-1.7 Pa

Ar: Air partial pressure ranging from 45:1 to 45:10

Results

HIPIMS Discharge



Peak voltage and current as a function of the air flow introduced in the plasma reactor.

Constant current could not be obtained for all air flows. Variation was between 3 and 6 A.

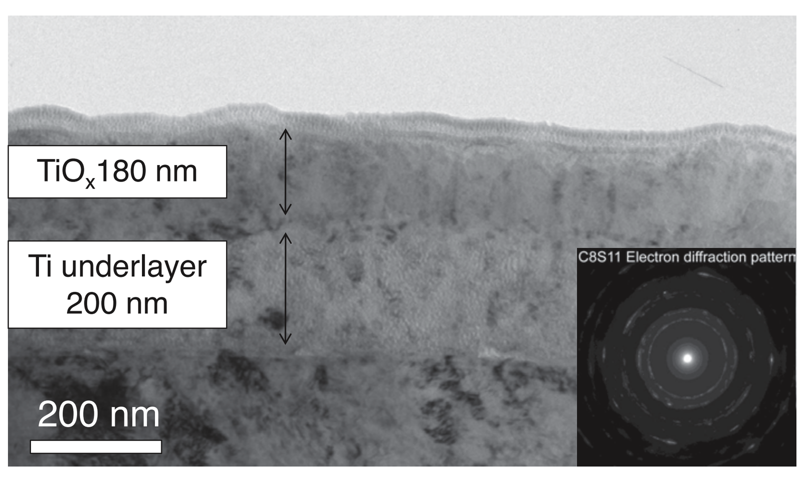
Voltage increased and current decreased as a result of target poisoning.

The content of Oxygen and Nitrogen increased in the plasma discharge as a function of the air flow.

For oxide mode the percentage of Oxygen in the chamber is around 5% whereas Nitrogen is 25%.

The deposition rate decreased as a function of the air flow due to target poisoning.

X-TEM (Cross sectional) Microstructure Analysis

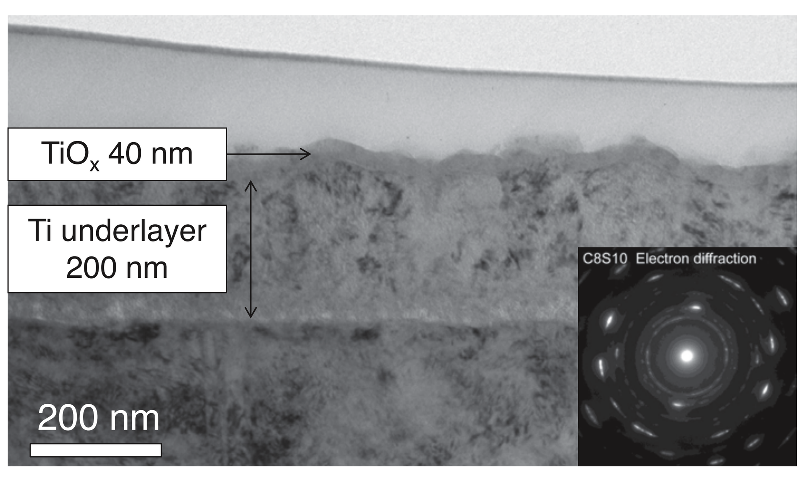


2 sccm air metallic mode

The coating is highly crystalline and very dense. The grains are randomly orientated with size of 70-100 nm.

The presence of the stable TiO_2 phases (rutile and anatase) can be excluded.

Film porosity is 1.5% over 1 cm^2 as estimated from Linear Scan Voltammetry.



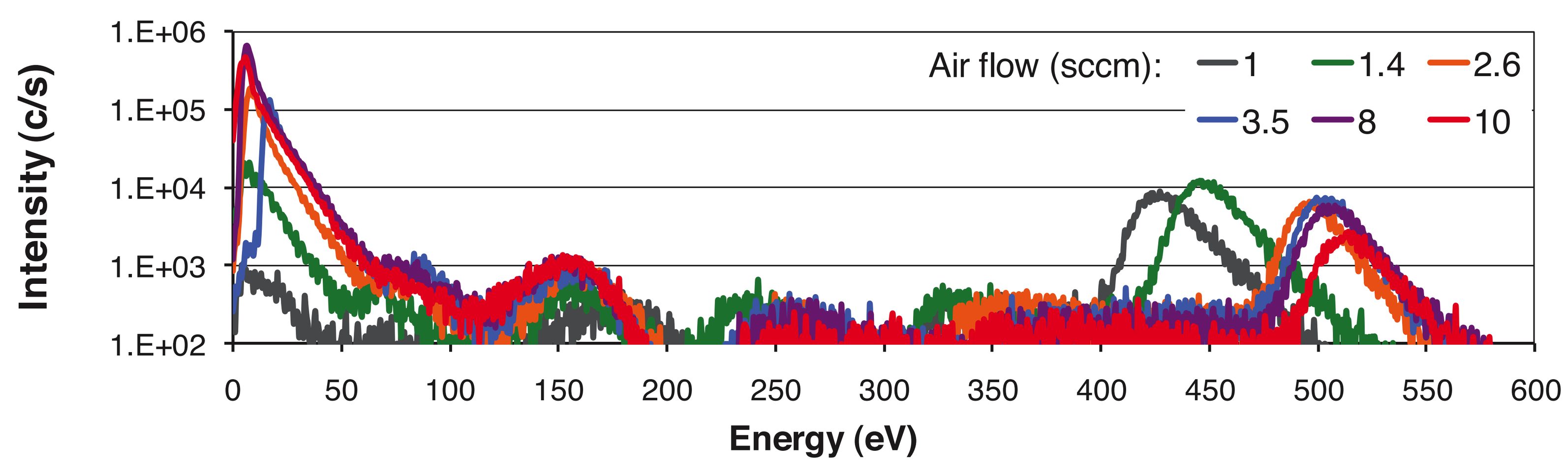
10 sccm air oxide mode

The coating appears crystalline in the diffraction pattern and very dense. The coating morphology follows the rough surface of the underlayer.

Film porosity is 2.5% over 1 as cm^2 as estimated from Linear Scan Voltammetry.

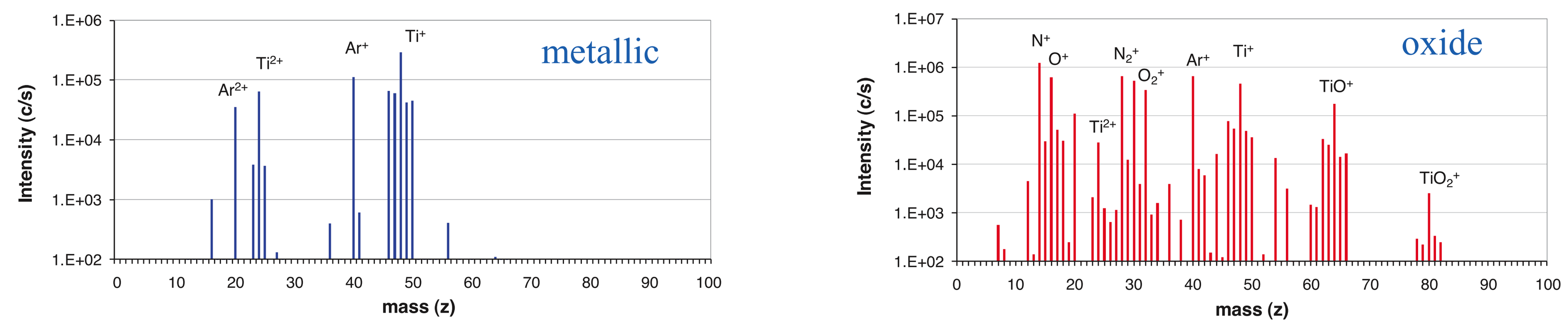
Mass spectrometry results:

Negative Ion Energy: O^-

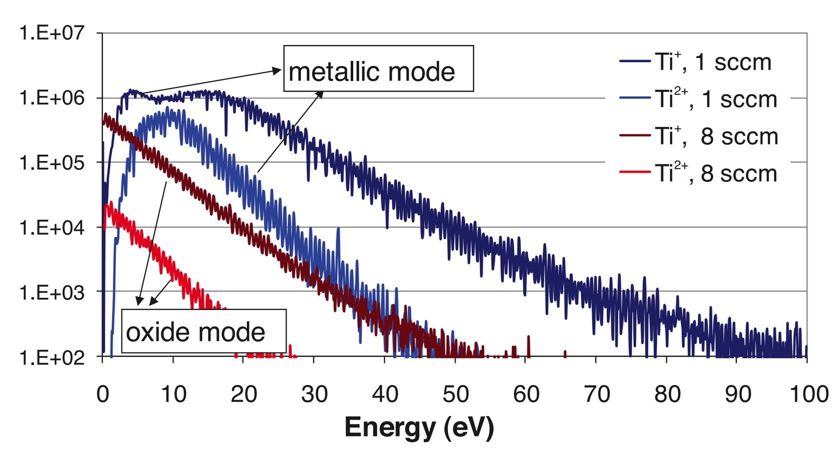


Ion content data from the IEDF (Ion Energy Distribution function) for negative ions obtained by mass spectrometry. Majority of ions observed are O^-, the high-energetic tail represents negative ions, O^-, which have been created close to the target. The detailed study of the energy distribution of O^- and O_2^- shows high-energy ions formed at the cathode with energies proportional to the full cathode voltage. The IEDF shows that in the transition from metallic to the oxide mode there is about 100 V drop of the voltage on the oxide surface layer on the cathode; this corresponds well with the measured cathode voltage.

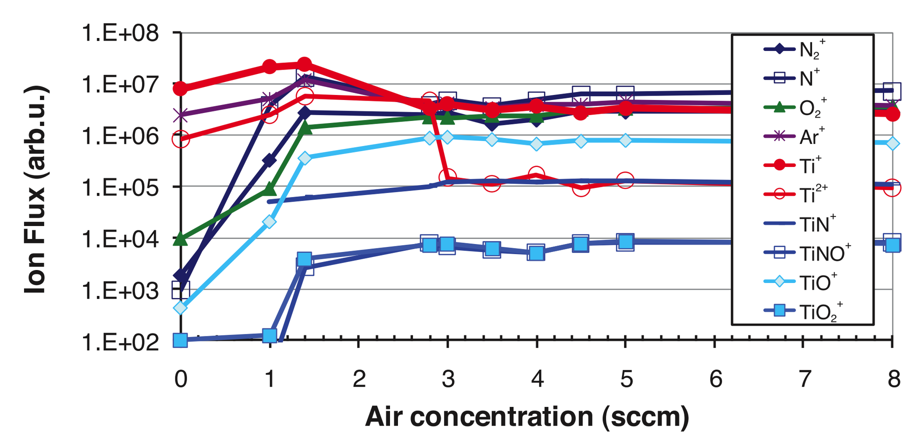
Mass spectra of positive ions in metallic and oxide mode:



Mass spectrometry measurements: *Ion Energy and Ion flux with respect to different concentrations of air in the discharge*



IEDF for Ti^+ and Ti^{2+}. Energy of the ions changes with air concentration. Note, 1 sccm contains 1.18% O_2 and 5.7% N_2 and 8 sccm contains 5.7% O_2 and 22.8% N_2. Ions with energy of more than 90 eV are observed at 1 sccm whereas the ion energy reduces to its half with 8 sccm i.e. in oxide mode.



Mass spectrometry measurements showed that the reactive HIPIMS discharge produced a deposition flux with a significant increased content of ionised film-forming species, such as Ti^+, Ti^{2+}, N^+, O^+, TiO^+ and TiO_2^+. Increasing the air content in the discharge resulted in an enhanced activation of the oxide species, TiO^+ and TiO_2^+, and reduction in the atomic ion N^+, Ti^+ and Ti^{2+}. Noticeable change in Ti^{2+} intensity by increasing the air concentration at 3 sccm (2.75% O_2 and 11.55% N_2).

Conclusions

The composition and energy of the ion flux in HIPIMS of Ti was investigated quantitatively in reactive mixture of Ar with increments in air composition. The detailed study of the energy distribution of O^- shows high-energy ions formed at the cathode with energies proportional to the full cathode voltage. Increasing the air content in the discharge resulted in an enhanced activation of the oxide species, TiO^+ and TiO_2^+, and a reduction in the atomic ion N^+, Ti^+ and especially Ti^{2+}. The ion energy is reduced significantly from the metallic to oxide mode.

Films deposited with HIPIMS in reactive atmosphere for metallic and oxide mode were analysed by TEM. Samples deposited in metallic mode present a very dense polycrystalline and columnar structure but no TiO_2 phase is formed. In oxide mode a high density crystalline films is formed. The porosity over large area ranges from 1.5 to 2.6%.

Acknowledgments

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References

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