

TIME RESOLVED STUDY OF THE HIPIMS POST-DISCHARGE

S. CUYNET^{1*}, M. PALMUCCI², A. CAILLARD¹, T. LECAS¹, A.L. THOMANN¹, P. BRAULT¹, J. BIGARRÉ³, P. BUVAT³

¹Groupe de Recherches sur l'Energétique des Milieux Ionisés (GREMI) CNRS UMR7344, Université d'Orléans, BP6744, 14 rue d'Issoudun, 45067 Orléans, France

² Materia Nova Research Center, Parc Initialis, Avenue N. Copernic 1, B-7000 Mons, Belgium

³ CEA, DAM, Le Ripault, BP 16, 37 260 Monts, France

*Corresponding author e-mail: stephane.cuyenet@univ-orleans.fr

ABSTRACT

This study deals with the investigation of post-discharges resulting from a pulsed magnetron sputtering process. To vary the working conditions in a large range, different sputtering targets and gases are used. The diagnosis of the post-discharge is mainly achieved by a Retarded Field Energy Analyzer (RFEA) and a mass spectrometer. These two techniques enable time resolved characterization of the post-discharge. The study will focus on the ion beam collected under specific HiPIMS regimes as well as the influence of the sputtering target material.

1. INTRODUCTION

High Power Impulse Magnetron sputtering (HiPIMS) sources tend to be commonly used in industrial physical vapor deposition processes, which require high reliability for thin layer deposition. HiPIMS is a pulsed direct current magnetron sputtering (DCMS) technique utilizing high peak power densities of typically several kilowatts per square centimetre at a low repetition frequency. The specific sputtering regime in HiPIMS mode allows the production of a dense ionized metallic vapour, which is not the case with pulsed DCMS. Some authors report a ratio of ionized species up to 70 % in HiPIMS processes [1,2]. This ratio, obviously, depends on numerous experimental parameters, but also of the sputtered target nature.

The present study focuses on sputtered materials with catalytic properties. The sputtering of two targets is investigated: platinum and gold. The main interest lies on the study of charged species

presence in the afterglow which may play a role on the final properties of the catalyst deposited on its support. Because of a particular magnetic topology, magnetron sputtering involves a very localized and confined plasma near the target during the discharge. Post-discharge is defined here as the place where the substrate is usually located, several cm away from the target. At this location the plasma is in a recombination state.

2. EXPERIMENTAL SETUP

Here, the sputtered 2" targets are made of pure platinum (99.99%) and pure gold (99.99%).

The HiPIMS power source used is a Hüttinger TPHP 4002. It is characterized by its ability to deliver a maximum voltage of -2000 V with a maximum peak power of 2 MW for a 10 kW time average power. Pulse duration can reach 200 μ s with a maximal frequency of 500 Hz. This power supply is connected to a slightly unbalanced 2" magnetron. Here, the impulse power is fixed at -1300 V, starts at $t = 0$ s and stops 100 μ s later. A vacuum of 10^{-7} mbar into the chamber is provided with a serial connection of a primary pump and an Adixen ATH500M turbo-molecular pump. In this study, the argon pressure is fixed to 1 Pa.

The electrical characteristics developed at the target are measured by a Stangenes broad band current probe and a Tektronix voltage probe.

The analysis of the post-discharge is performed via two methods. The first is conducted with a homemade Retarding Field Energy Analyzer (RFEA). It is sized to work in conditions allowing the recording of time-resolved measurements, while maintaining a good signal to noise ratio. The analyzer consists of four grids

and a current collector. The first grid is grounded. The discriminator grid voltage is tuned between 0 V and 65 V with a voltage step of 0.1 V. The current collected by the collector plate is amplified by solid state electronics components.

The second method used to analyze the post-discharge is mass spectrometry. The mass spectrometer used was a Hiden HAL 7 EQP HIGH ENERGY. Measurements are made by coupling a quadrupole filter (2500 amu) and an electrostatic energy analyzer sector of 45 ° giving an accuracy of 0.25 eV. The orifice of the spectrometer is located at the same distance as the one used for RFEA measurements.

3. RESULTS AND DISCUSSION

The voltage and current characteristics are recorded for each target and plotted in Figure 1. The high power impulse is triggered at $t_{\text{HiPIMS}} = 0$ and lasts 100 microseconds at the desired voltage. Beyond 100 microseconds, the voltage drops gradually: the generator manages here the decrease of the voltage in order not to leave the pre-ionization threshold. The corresponding behavior will directly depend on the discharge conditions as the nature of the gas, the operating pressure and the nature of the target.

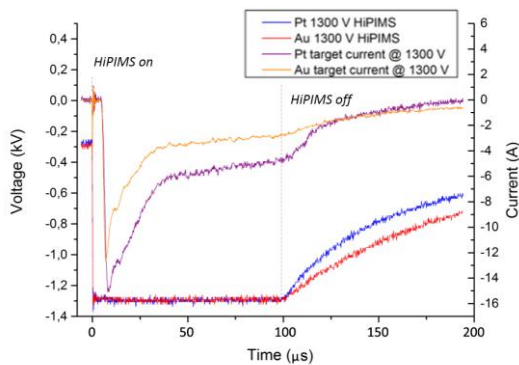


Figure 1 Electrical characteristics of the HiPIMS discharge for Pt and Au targets

Currents on both targets have similar appearance with a first phase where the current collected on the target increases sharply and then decreases rapidly until a pseudo-plateau is reached. Some authors attribute this phenomenon to a rarefaction of the gas (here Ar) at the target surface, which furthers the self-sputtering process [3].

Be noted that in spite of a target voltage equivalent of -1300 V, the current on the gold target is lower than that on the platinum target. This difference reaches a factor of 2 on the pseudo-plateau.

Despite of very similar masses and identical sputtering conditions, both targets will be sputtered differently. This reflects the importance of ionization mechanisms and sputtering rate of each material.

RFEA measurements of the post-discharge confirm these trends since results are also very different. Figure 2 shows the energy distribution of the species that compose the post-discharge at a distance of 50 mm from a platinum target and a gold target. The measures begin 5 microseconds before the starting of the HiPIMS and ends 200 microseconds later. The fine variations (0.1 V) of the potential of the analyzer discriminative grid give a very accurate reading of the current collected on the analyzer collector.

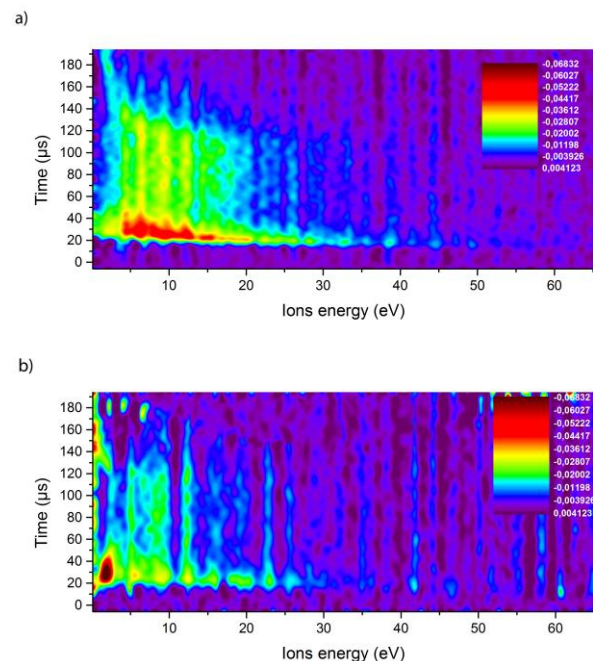


Figure 2 (a) Pt and (b) Au mapping of the different energy distributions during the -1300 V HiPIMS discharge. The unit of the colour chart is express as dI_C/dV_D .

By performing the derivative of this current for each time, depending on the discriminative grid voltage, we obtain a time resolved mapping of the energy distributions. Besides the fact that the intensities of the distributions are lower with gold than with platinum, both maps show several peaks of energy. Despite a quite good discrimination between these ones, it is impossible at this level to identify the different ionic species.

The identification of the nature of ions coming from the plasma is carried out by mass spectrometry. This method allows to determine the mass and the kinetic energy of the plasma ions. Figure 3 provides information on the nature of the various ions that are collected at 50 mm from the target. For the sputtering of the platinum target, like for the gold one, metallic ions with one or two charges are detected. In both cases the singly and doubly charged argon are also present.

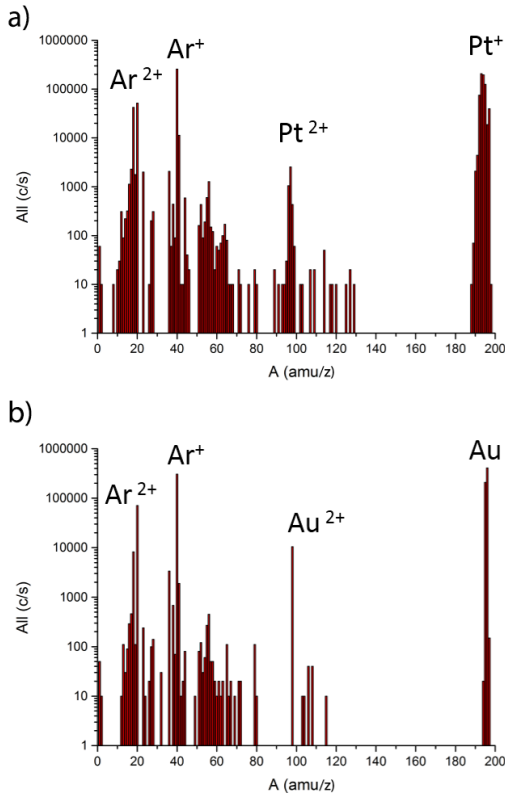


Fig. 3 Mass spectra of the different species for (a) Pt and (b) Au sputtering without time resolution.

For comparison with previous results obtained with the energy analyser, the mass spectrometry measurements are pursued by a study of the

composition of the post-discharge at two detection times with a gate of 10 microseconds for each. It is noted ($t_{MS} = 0$) as a reference of the first moments of detection for each mentioned ions. Figure 4 summarizes the data obtained at the early time, i.e. 10 microseconds after ($t_{MS} = 0$). The ionization of argon gas produces two distinct energy distributions. This result is found for the single and double charges of argon, whatever the target material. The energy distribution of the metal ions exhibits a single peak. Width of the distributions is different depending on the sputtered material. It should be noted that platinum doubly charged ions, are more energetic than gold ones.

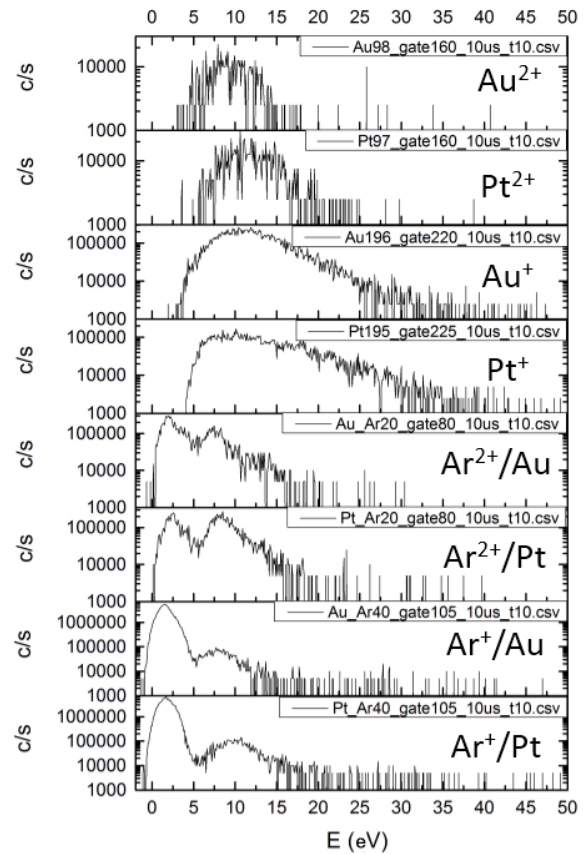


Fig. 4 Mass spectra of the different species for Pt and Au sputtering at 10 μ s after first detection of ions.

Figure 5 gives the values measured under the same conditions as above, but about 50 microseconds after ($t = 0$). The results confirm some of the first observations on the energetic distributions of metal ions. It can be noted that the maxima of the distributions tend to move towards lower initial energy values. Moreover, the bimodal distribution of argon ions has disappeared in both cases. A merger of both distributions to form only one seems to favour a more stable state could be invoked. Overall, there is a decrease in the detection level of argon gas ions to the benefit of metallic ions. The combination of these results confirms the maximum position of most of the energy distributions of the ions collected by the RFEA.

4. CONCLUSION

The plasma species resulting from the sputtering of an Au and a Pt target by HiPIMS has been studied by a RFEA device. The intensities of the distributions are lower with gold than with platinum and both time resolved distributions show several peaks of energy. Because the identification of the ionic species is impossible with such equipment, time of flight mass spectrometry has been performed. In this case, the dimensions of the spectrometer introduce times of flight of detected species, and collision probabilities, which could not be neglected. It has been found that metal and argon ions are present in the plasma with different energy distributions. For $T_{MS} = 10$ ms, two energy peaks (centered around 2 and 8 eV) are observed for singly and doubly charged argon ions and the singly charged metal ions display a unique broad peak with a maximum at about 10 eV and upper energy close to 40 eV. For $T_{MS}=50$ ms, the energy of the argon ions decreases and the distributions are centered at few eV. For singly charged metal ions, large energies are still visible even if the distributions reach a maximum at about 6 eV. The RFEA energy peaks ranging from 0 to 40 eV result of the superposition of argon and metal ions energy distribution centered at different energy values. Below 5 eV, the RFEA signal mainly comes from gas argon ions. Between 5 and 20 eV, metal and argon ions are both present and only singly charged metal ions are responsible for the RFEA collected current above 20 eV.

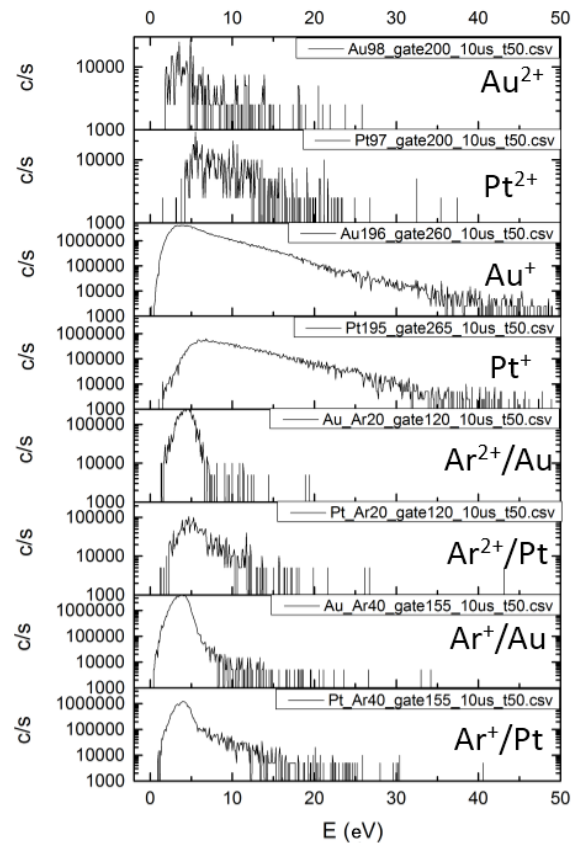


Fig. 5 Mass spectra of the different species for Pt and Au sputtering at 50 μ s after first detections of ions.

REFERENCES

- [1] M. Samuelsson, D. Lundin, J. Jensen, M. A. Raadu, J. T. Gudmundsson, U. Helmersson, "On the film density using high power impulse magnetron sputtering", *Surface and Coatings Technology* **205**, 591–596 (2010).
- [2] J. Bohlmark, J. Alami, C. Christou, A.P. Ehasarian, and U. Helmersson, "Ionization of sputtered metals in high power pulsed magnetron sputtering" *Journal of Vacuum Science & Technology A : Vacuum, Surfaces, and Films* **23**, 18 (2005).
- [3] A. Anders, "High power impulse magnetron sputtering and related discharges: Scalable plasma sources for plasma-based ion implantation and deposition". *Surface and Coatings Technology*, **204**, 2864–2868 (2010).