

# Transport and Deposition of Plasma-Sputtered Platinum Atoms: Comparison Between Experiments and Simulation

Amaël Caillard, Christine Charles, Rod W. Boswell, and Pascal Brault

**Abstract**—The deposition of platinum atoms by argon plasma sputtering has been simulated by using a 3-D Monte Carlo simulation called Sputtered Particles Transport in Gas, which provides spatial and energy distributions of the Pt atoms impinging on the substrate and on the chamber walls. The Yamamura formula provides the Pt sputtering yield from argon ions, whereas the initial energy distribution of sputtered atoms is given by the Thompson distribution. The Pt flux on the chamber walls and on the substrate are compared with experimental deposition rates.

**Index Terms**—Deposition, Monte Carlo, plasma sputtering, platinum.

PLATINUM deposition by plasma sputtering has been recently used for the manufacture and the optimization of proton exchange membrane fuel cell electrodes [1] using plasma technology. For this application, the loss of this catalyst on the reactor's walls needs to be minimized due to its cost and its limited availability. A good uniformity of the catalyst deposition is necessary for an optimized and homogeneous electrochemical activity of the electrode. This paper reports on the numerical results and their comparison with experimental ones on the sputtering and deposition of Pt atoms on silicon substrate.

Platinum thin film has been deposited on silicon in a plasma processing chamber called Southern Cross. A low pressure argon plasma (a few microbars) is generated by a radio-frequency (RF, 13.56 MHz)-powered double saddle antenna placed around a 15-cm-diameter glass tube attached to the top of a diffusion chamber shaped as a cross (two perpendicular cylinders with an inner diameter of 30 cm and a length of 55 cm). Base pressure that is below  $5 \times 10^{-6}$  mbar was achieved by a primary/turbomolecular pump combination. Three solenoids surrounding the source and the diffusion chamber provide a magnetic field (about 80 G along the vertical axis  $z$ ) which is adjusted to maximize the argon ion flux impinging on the Pt target. The negatively dc-biased Pt target ( $50 \times 50 \times 0.1$  mm) is placed in the diffusion chamber that is 10 cm below the heli-

con source and on the vertical axis ( $z = -10$  cm,  $R = 0$  cm). Two different substrate holders are used for this paper. The first one is a 72-mm-diameter circular substrate holder that is perpendicular to the Pt target ( $z = -20$  cm) and off the vertical axis ( $R = 6.5$  cm). The second is a horizontal semiannulus substrate holder which is fixed around the Pt target ( $z = -10$  cm). The distance between the semiannulus substrate holder and the target's center is 10 cm. Several pieces of silicon ( $10 \times 10$  mm) are stuck on these two substrate holders.

During the experiment, the argon pressure and the dc bias applied to the target are fixed to 5  $\mu$ bar and  $-300$  V, respectively. The input RF power is adjusted during the deposition to keep a constant current of 30 mA on the target face that is opposite to the substrate holders. After a deposition time of 30 min, the amount of platinum (express in  $10^{15}$  atoms/cm<sup>2</sup>) deposited on each piece of silicon is determined by Rutherford backscattering spectroscopy. Langmuir probe measurements at the target position are employed to determine the plasma potential ( $V_p$ ), the electron density ( $n_e$ ), and the electron temperature ( $T_e$ ). Typical values are  $V_p = 15$  eV,  $n_e = 10^{11}$  cm<sup>-3</sup>, and  $T_e = 4$  eV.

The deposition process can be split into four parts:

- 1) Energetic bombardment of argon ions on the Pt target;
- 2) Ejection of the sputtered particles from the Pt target;
- 3) Transport of the Pt sputtered particles through the gas;
- 4) Sticking of Pt atoms on the substrate.

The mean energy of the argon ions reaching the Pt target is assumed to be  $\alpha \times (300 + V_p)$ , where  $\alpha$  is a constant, describing energy losses by collisions in the thin sheath between the plasma and the target surface. For the present experimental conditions,  $\alpha$  was estimated to 0.76, using Monte-Carlo modeling [2]. The flux of the argon ions is assumed to be homogenous on the target, and their mean ion energy is deduced to be 240 eV.

Pt atoms ejected from one target's face have been investigated by numerical and analytical models. On the target surface, the energy distribution of the sputtered Pt atoms can be deduced by using the Thompson energy distribution  $f_{\text{THOMPSON}}$  [3], whereas the sputtering yield (number of Pt atom per incident argon ion) is estimated to be 0.61 by using the Yamamura formula at normal incidence [4].

The Sputtered Particles Transport in Gas (SPaTinG) simulation includes the collisional transport of the Pt atoms traveling through the argon gas between the target and substrate, allowing one to determine the energy and spatial distribution of Pt atoms reaching the substrate. In total,  $5 \times 10^6$  Pt sputtered

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A. Caillard, C. Charles, and R. W. Boswell are with the Space Plasma, Power and Propulsion, Research School of Physical Sciences and Engineering, The Australian National University, Canberra, ACT 0200, Australia (e-mail: ama112@rsphysse.anu.edu.au; christine.charles@anu.edu.au; rod.boswell@anu.edu.au).

P. Brault is with the Groupe de Recherche sur l'Energétique des Milieux Ionisés, UMR6606 Université d'Orléans-CNRS Polytech'Orléans BP6744, F-45067 Orléans Cedex 2, France (e-mail: Pascal.Brault@univ-orleans.fr).

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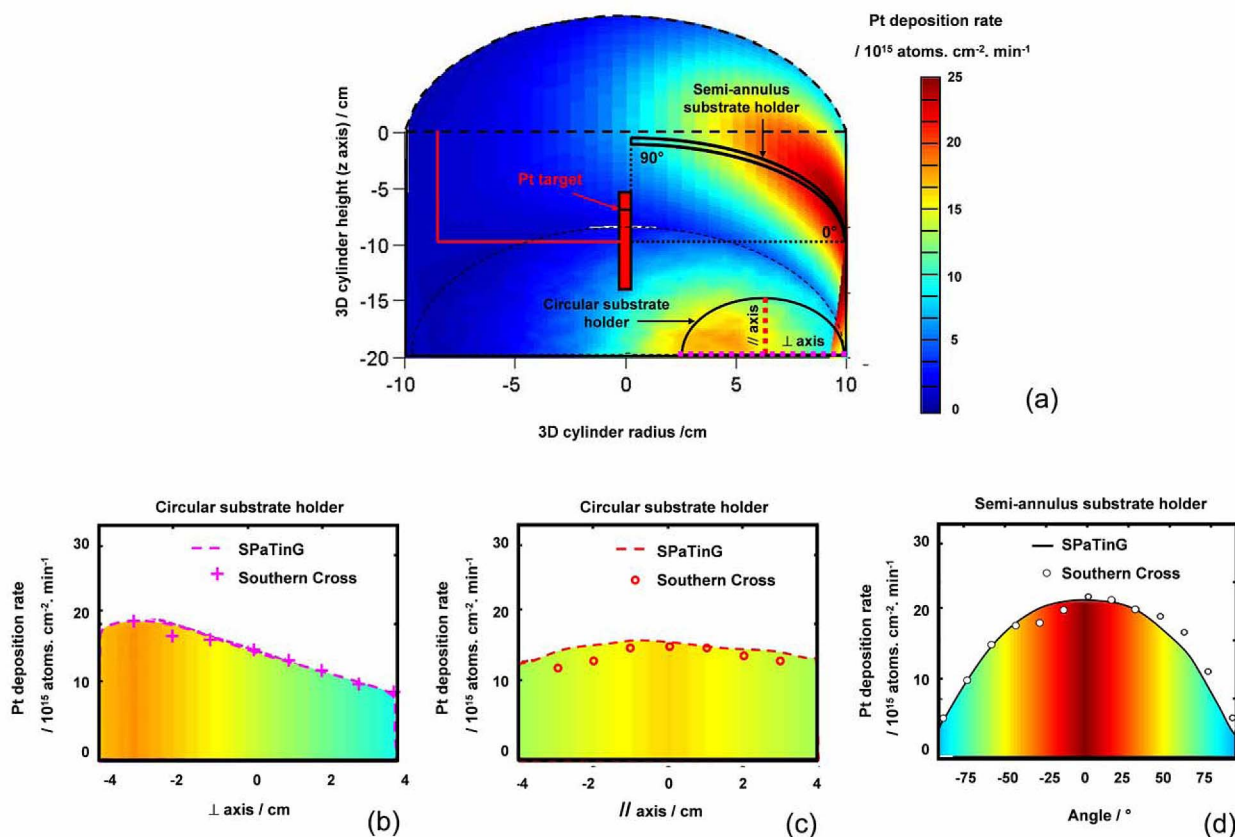


Fig. 1. (a) Simulation of Pt atoms deposited on a 3-D cylinder (half of the cylinder is shown). Comparison between experimental and simulated results (b) along the substrate axis ( $z = -20$  cm) that is perpendicular to the target, (c) along the substrate axis ( $z = -20$  cm) that is parallel to the target, and (d) on the horizontal semiannulus substrate holder placed at 10 cm from the center of the target ( $z = -10$  cm).

atoms were randomly generated on the target surface; however, each atom has been treated separately in the simulation. The initial energy and the ejection angles are randomly determined from the Thompson and the cosine  $\cos^{0.8}$  [5] distributions. Subsequently, the program follows the trajectory of the atom from its ejection, which is through a series of collisions, to one of the chamber walls or the substrate surface. We only consider the Pt atom–argon atom interactions, where the argon atoms are assumed to be immobile and at room temperature. We assume that inelastic collisions and elastic collision Pt atom–Pt atom are insignificant. Collision events are modeled by scattering in a Lennard Jones potential. The mean free path between successive collisions is randomly generated, and the scattering angle in the plane of the collision is calculated by using the Landau formula [6].

The sticking coefficient for Pt atoms on silicon has been previously estimated to be around 0.33 [5].

Finally, Fig. 1(a) shows the simulated deposition rate (expressed in  $10^{15}$  atoms · cm<sup>-2</sup> · min<sup>-1</sup>) on a silicon cylinder with an inner diameter of 20 cm and a length of 20 cm. The target is placed in the center. The experimental deposition rate has been compared with the simulated flux of Pt atoms impinging on the two substrate holders using SPaTinG. The bottom and circular walls of the simulated cylinder mimic the semiannulus substrate holder [Fig. 1(d)] and the circular sub-

strate holder in the experiment [Fig. 1(b) and (c)], respectively. A good agreement between the simulation and the experience in Southern Cross is obtained for each graph.

In summary, platinum deposition by plasma sputtering has been simulated with the use of the SPaTinG program. The simulated deposition rates agree well with the experimental results. This simulation can be used to quantify the Pt deposition loss on the system's wall and the homogeneity of the Pt deposition on the substrate. It supplies elements of reflections for the conception of deposition reactor for the manufacture of fuel cell electrodes.

## REFERENCES

- [1] A. Caillard, C. Charles, R. Boswell, P. Brault, and C. Coutanceau, "Plasma based platinum nanoaggregates deposited on carbon nanofibers improve fuel cell efficiency," *Appl. Phys. Lett.*, vol. 90, no. 22, p. 223 119, Jun. 2007
- [2] A. Meige and N. Plihon, "Propagating double layers in electronegative plasmas," *Phys. Plas.*, vol. 14, p. 053 508, Mar. 2007.
- [3] D. A. Thompson, "Application of an extended linear cascade model to the sputtering of Ag, Au and Pt by heavy atomic and molecular ions," *J. Appl. Phys.*, vol. 52, no. 2, pp. 982–989, Feb. 1981.
- [4] Y. Yamamura and H. Tawara, "Energy dependence of ion-induced sputtering yields from monatomic solids at normal incidence," *At. Data Nucl. Data Tables*, vol. 62, no. 2, pp. 149–253, Mar. 1996.
- [5] A. Caillard, "Elaboration d'électrodes de piles à combustible par plasma," Ph.D. dissertation, Australian Nat. Univ. Canberra, Australia and Université d'Orléans, Orléans, France, 2006.
- [6] L. D. Landau and E. M. Lifshitz, *Mechanics*. London, U.K.: Pergamon, 1976, p. 48.