A Low Temperature Synthesis of Electrochemical Active Pt Nanoparticles and Thin Films by Atomic Layer Deposition on Si(111) and Glassy Carbon Surfaces

Rui Liu,^a Lihao Han,^{a,b} Zhuangqun Huang,^{a,d} Ivonne M. Ferrer,^a Arno H.M. Smets,^b Miro Zeman,^b Bruce S. Brunschwig^{,c} and Nathan S. Lewis^{*,a,c,d,e}*

^a Joint Center for Artificial Photosynthesis, California Institute of Technology, Pasadena, CA 91125, United States.

^b Photovoltaic Materials and Devices (PVMD) Laboratory, Delft University of Technology, P.O. Box 5031, 2600 GA Delft, Netherlands.

^c Beckman Institute, California Institute of Technology, Pasadena, CA 91125, United States.

^d Division of Chemistry and Chemical Engineering, 210 Noyes Laboratory 127-72, California Institute of Technology, Pasadena, CA 91125, United States

^e Kavli Nanoscience Institute, California Institute of Technology, Pasadena, CA, 91125, USA

KEYWORDS: Atomic layer deposition, Pt nanoparticles; Pt thin films, Water splitting, Hydrogen Evolution

ABSTRACT

Atomic layer deposition (ALD) was used to deposit nanoparticles and thin films of Pt onto etched p-type Si(111) wafers and glassy carbon discs. Using precursors of MeCpPtMe₃ and ozone and a temperature window of 200–300 °C the growth rate was 80 – 110 pm/cycle. X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and scanning-electron microscopy (SEM) were used to analyze the composition, structure, morphology and thickness of the ALD-grown Pt nanoparticle films. The catalytic activity of the ALD-grown Pt for the hydrogen-evolution reaction was shown to be equivalent to that of e-beam evaporated Pt on glassy carbon electrode.

Introduction

The efficient operation of a photoelectrochemical solar fuels generator based on water-splitting requires catalysts to facilitate charge-transfer reactions at the interface between the semiconducting light absorbers and the electrolyte. The preferred catalysts of the hydrogen-evolution reaction (HER) are metals and metal alloys, which can be deposited onto the photocathodes of photoelectrochemical cells either as nanoparticles (NPs) or as thin films [1-3]. Platinum is the archetypal catalyst for the HER because Pt exhibits a relatively low overpotential (< 40 mV) to drive the HER at a current density of 10 mA cm^{-2} [1, 4-6]. The deposition of catalytically active metals onto a semiconductor electrode surface, such that it preserves the electronic properties of the semiconductor/liquid junction, is an important step in the development of a photoelectrochemical water-splitting device.

Thin films of Pt, with thicknesses from a few to tens of nm, can be deposited onto surfaces by sputtering [7], electron-beam evaporation [8], chemical vapor deposition (CVD) [9], or electrochemical deposition [1]. Nevertheless, a method that allows deposition of highly catalytic Pt films of readily controlled thickness without the use of high temperatures or a high-vacuum environment is desirable. Atomic-layer deposition (ALD) has been widely employed to grow thin-film metal-oxide light absorbers [10-12], to deposit protective layers [13, 14] onto surfaces, and to deposit catalysts onto photoelectrodes [15, 16]. ALD provides facile control over the thickness of the deposited films, produces films with excellent uniformity, and can be applied to structures with high surface areas. ALD also offers the advantage of being a relatively low-temperature process that does not require a high-vacuum environment or post-deposition annealing. Pt nanoparticles have been deposited onto a TiO_2 -coated Si nanowire structure used in a water-splitting device by ALD using (trimethyl)methylcyclopentadienylplatinum(IV)

(MeCpPtMe₃) and oxygen gas as precursors [17]. Similar Pt nanoparticles, grown by ALD using the same precursors, have been deposited on Si nanowires as catalysts for sunlight-driven HER [18]. In both cases, 10–50 cycles of growth were required to deposit nanoparticles ~2–3 nm in diameter with surface coverages in the low sub-monolayer range [17, 18]. The wider use of ALD for deposition of Pt has been limited by either slow growth rates (< 50 pm/cycle) or high temperatures (typically 250–350 °C) [17–22]. Although Pt ALD growths with ozone as oxidizer were achieved at temperatures as low as 120–140 °C, the growth rate was only ~ 30 pm/cycle [21, 23, 24]. Faster growth rates at low growth temperature for metallic Pt ALD growth are desirable.

Herein we describe an ALD method to deposit Pt NPs or thin films onto p-type Si wafers or carbon discs. The use of MeCpPtMe₃ and ozone as precursors at temperatures of 200–300 °C gave growth rates of 80 – 110 pm/cycle. Very recently, improved rates of ALD growth (70 pm/cycle) of Pt have been reported using the same precursors on oxidized Si(0001) surfaces [25][26]. Our work complements these results by including characterization of the electrocatalytic activity of the ALD Pt films on glassy carbon rotating disk electrodes. X-ray photoelectron spectroscopy (XPS), atomic-force microscopy (AFM), and scanning-electron microscopy (SEM) were used to analyze the composition, structure, morphology and thickness of the ALD-grown Pt materials.

Experimental Details

A. Preparation of substrates

Boron-doped p-type Si(111) wafers with a resistivity of 20 Ω•cm (Silicon Resource Company) were cleaned using an RCA1 procedure by soaking in a 5:1:1 (by volume) solution of deionized water, ammonium hydroxide (27 %, Sigma Aldrich), and hydrogen peroxide (30 %, Sigma Aldrich) for 10 min. The wafers were rinsed with deionized water, immersed in an RCA2

solution, 5:1:1 (by volume) deionized water, hydrochloric acid (27 %, Sigma Aldrich), and hydrogen peroxide (30 %, Sigma Aldrich) for 10 min, and then immersed in an aqueous NH_4F solution (40 %, Sigma Aldrich) for 30-40 min to obtain H-terminated, terraced surfaces. A stream of nitrogen was used to dry the wafers, which were then immediately transferred into the ALD chamber for metal deposition.

Five mm in diameter and 4 mm thick glassy carbon disks (Sigradur G, HTW Hochtemperatur-Westoff GmbH) were polished with 600 grit Carbimet SiC paper (Buehler) at 150 rpm for 1 min using a Stuers LaboPol-5 polisher, and then immersed in 1.5 M HNO_3 (69 % HNO_3 , Sigma Aldrich). The disks were then polished at 150 rpm using an MD-Floc synthetic nap polishing pad (Stuers) and a sequence of diamond slurries (9, 6, 3, 1 and 0.1 mm MetaDi Supreme, Buehler) for 1 min each. After polishing, the disks were sonicated sequentially for 10 min each in water, acetone, isopropanol, and water.

B. Atomic-layer deposition of Pt

Pt deposition was performed using a Savannah ALD system (Cambridge Nanotech). The substrates were heated to 200–300 °C in a chamber held at a constant pressure of 26.7–40.0 Pa. The (trimethyl)methylcyclopentadienylplatinum(IV), MeCpPtMe_3 (Strem Chemicals, 99 % pure), precursor was heated to 75 °C and was swept into the ALD chamber using four equal consecutive pulses of $\text{N}_2(\text{g})$ at a flow rate of 10 sccm. The MeCpPtMe_3 was then purged from the system for 10 s using nitrogen gas, after which ozone (O_3) from the ozone generator (LG-7, Del Ozone, California, USA) built into the ALD system was admitted for 0.1 s. The ozone generator system delivers 120 mg/L of ozone in O_2 (~7 % O_3 by weight). The pulses of precursors were delivered with the stop valve close to isolated the growth chamber from the vacuum pump. The duration of the exposure of the substrate to the MeCpPtMe_3 precursor was varied, in the range of

0.25–1.5 s per cycle, to determine the dependence of the growth rate on exposure time. Either 15, 20, 25, 35, 50 or 100 cycles of ALD growth were used, to obtain films with varied thicknesses and morphologies. Upon completion of the ALD growth, the samples were removed from the chamber and stored under ambient conditions until analyzed.

To determine the rate of growth of the Pt films as a function of the duration of precursor exposure, the samples were removed from the ALD chamber after every 50 cycles of growth and the thickness of the film was determined using ellipsometry. The ellipsometry (α -SE, J.A. Woollam Co. Inc.), data were collected with the incident beam and detector located at either 60 °, 65 ° or 70 ° relative to the surface normal. The samples were then reloaded into the ALD chamber for additional cycles of growth.

C. Deposition of Pt films by electron-beam evaporation

Electron-beam evaporation of Pt onto fully assembled electrodes was performed under vacuum using a Denton Explorer evaporator system with a base pressure of $< 1.33 \times 10^{-3}$ Pa. The Pt (Kurt J. Lesker, 99.99 %) was deposited at a rate of 10 – 100 pm s⁻¹ to a thickness of ~ 3 nm.

D. Characterization of deposited Pt films

An atomic-force microscope (Dimension-Icon, Bruker Corp.) with a Nanoscope V controller was used to collect and analyze images of the deposited Pt films and substrates. X-ray photoelectron spectra (XPS) were collected using a Surface Science M-Probe Spectrometer, controlled by Hawk Data Collection software (Service Physics, Bend OR; V7.04.04). The Al K α line at 1486.6 eV was used for excitation. Ar-ion etching of each sample was performed in the XPS chamber for 45 s prior to the collection of spectra, to remove any adsorbed moisture, O₂ or CO₂.

Scanning-electron microscopy was performed using a Nova NanoSEM 450 with an accelerating voltage of 15 kV.

E. Electrochemistry

Rotating-disk voltammetry was performed using the samples prepared on the carbon-disk substrates. The carbon-disk samples were mounted in an E-6 series ChangeDisk rotating disk electrode assembly (Pine Instrument Company). A conventional three-electrode configuration was employed in a modified U-cell, based on a previously published experimental procedure. Briefly, the U-cell consisted of two chambers separated by a fine-porosity glass frit. One chamber contained ~120 mL of 1.0 M H₂SO₄(aq), the carbon-disk working electrode, and a saturated calomel reference electrode (SCE, CH Instruments) that was calibrated against dilute ferrocene monocarboxylic acid (Sigma Aldrich, 97 % pure) in 0.2 M phosphate buffer (pH 7, BioUltra) prior to use. The other chamber contained ~25 mL of 1.0 M H₂SO₄ and a carbon rod (Alfa Aesar, 99.99 % pure) auxiliary electrode. An MSR rotator (Pine Instrument Company) was used to rotate the working electrode at 1600 RPM during the electrochemical measurements. The electrolyte was purged for 30 min with hydrogen (UHP, Air Liquide) prior to measurements, and hydrogen was continuously bubbled through the electrolyte during measurements. The electrodes were controlled by a Bio-Logic SP200 potentiostat-galvanostat, and the data were collected and analyzed using the Bio-Logic EC-Lab software. The surface area of each rotating disk electrode that was exposed to the electrolyte was 0.195 cm².

Results

A. Growth rate and film morphology

Boron-doped p-type Si(111) wafers were prepared by cleaning with RCA1 & RCA2, then rinsed and etched with NH_4F to obtain H-terminated, terraced surfaces [27]. The wafers were dried and immediately transferred into the ALD chamber for metal deposition. Figure 1a shows the dependence of the growth rate on the exposure time per growth cycle to the Pt precursor for deposition onto substrates held at 250 °C. Pt precursor exposures of ≤ 0.25 s/cycle only yielded scattered Pt NPs, while exposures of ≥ 1.0 s/cycle yielded films with growth rates exceeding 80 pm/cycle. The growth rates were highly reproducible across samples. Figure 1b shows the dependence of the growth rate on the temperature of the substrate, for growths using a precursor exposure of 1.0 s/cycle. For temperatures < 180 °C, growth rates decreased significantly and were difficult to estimate due to the low deposition of Pt. The rate of deposition did not increase at temperatures > 250 °C. Figure 1c shows the dependence of the thickness of the Pt films on the number of ALD cycles, for a substrate temperature of 250 °C and a precursor exposure of 1.0 s per growth cycle. There is an initial delay of film growth of ~ 30 cycles as observed for other noble metal ALD growth processes [28]. Under these growth conditions, after the initial delay, the thickness of the film increased at a constant rate of 110 ± 10 pm/cycle. Figure 1d image show SEM images of a cross-section of a Pt film on a Si(111) substrate. The film was obtained using a precursor exposure of 1.0 s per cycle for 500 cycles of growth at 250 °C, and was about 45 nm thick.

Figure 1. The ALD characteristics for Pt deposition on Si(111). (a) Dependence of the growth rate on Pt precursor exposure time for substrates held at 250 °C. The exposure time per growth cycle to the MeCpPtMe₃ precursor is shown on the x axis. (b) Dependence of the growth rate on the temperature of the substrate for growths using a precursor exposure time of 1.0 s/cycle. (c) Dependence of the Pt thickness on the total number of precursor exposure cycles for growths using a substrate temperature of 250 °C and a precursor exposure time of 1.0 s/cycle. An initial

delay in film growth of ~30 cycles was observed. (d) Cross-sectional SEM image of a 45 nm thick Pt film on a Si(111) substrate obtained from a growth at 250 °C with a precursor exposure time of 1.0 s/cycle for 500 cycles of growth. For Figure 1a and b growth rates were measured after 50 cycles and calculated using the total number of cycles including those of the initiation phase

AFM images showed that ALD growths of Pt films were preceded by the formation of Pt NPs (Figure 2). Images of the initial Si(111) surface, before ALD growth, showed smooth terraces with a roughness of < 0.20 nm (Figure 2a). Si terraces were still observable in AFM images after the deposition of Pt NPs (Figure 2b - d), suggesting that ozone did not significantly disturb the morphology of the surface. Differences in the size and orientation of the Si terraces shown in Figures 2 (a)-(c) were due to the different regions imaged. Both the number of the Pt NPs and the coverage of the substrate surface increased with the number of ALD cycles. The density, and height of the Pt NPs grew during the first 30 cycles, as measured by AFM topology scans (from 1.4 ± 0.1 nm high for 10 cycles to 3.5 ± 0.5 nm for 35 cycles). The Pt NPs started as clusters on the surface, and then with increasing growth cycles expanded into larger islands (Scheme 1), consistent with recent observations for ALD growth of Pt on highly oriented pyrolytic graphite [28]. For growths at 250 °C after 30 cycles, NPs with a diameter of ~ 3-4 nm fully covered the Si surface (Figure 2f), and the thickness of the film could be determined by ellipsometry. After 200 cycles of growth, the Pt film uniformly covered the silicon surface and exhibited a surface roughness of ~ 1 nm, consistent with the roughness measured by ellipsometry (~1.3 nm). Similar morphology changes were observed for Pt growth at temperatures between 200 and 300 °C.

Figure 2. AFM images of the surface morphologies of the NH_4F -etched Si(111) substrates with (a) 0, (b) 10, (c) 15, (d) 20, (e) 25, and (f) 35 ALD cycles of Pt deposition.

Scheme 1. Schematic illustration of the growth of Pt NPs on a substrate and the formation of a continuous film.

B. Surface characterization

A Pt film deposited on glassy carbon using 50 ALD cycles at 250 °C was characterized by XPS and SEM, and compared with a sample prepared using electron-beam evaporation, which was

expected to produce a Pt film with no organic material. A glassy carbon substrate was chosen for the XPS analysis, rather than a Si substrate, to avoid binding-energy shifts due to band bending at the Pt-Si interface. Figure 3 shows an SEM image of 50 cycles of ALD Pt on glassy carbon. The surface is fully covered by Pt; the dark strips on the surface are where the surface was deliberately scratched to show the glassy carbon underneath. The morphology of the Pt surface was similar to that observed for Pt on Si (Figures 1d). EDX analysis showed 0.1 ± 0.01 atomic% Pt for ALD (50 cycles) and e-beam (~ 3 nm) Pt samples.

Figure 3. A) SEM image and B) EDX of ALD Pt (50 cycles 250 °C) deposited on glassy carbon substrate. The dark lines on the right hand side of A are scratches in the Pt layer showing the glassy carbon substrate.

Figure 4. XPS showing the Pt $4f_{7/2}$ peak region for Pt films deposited by (a) electron-beam evaporated Pt film (~ 3 nm thick) and (b) of ALD (50 cycles at 250°C) Pt deposited on a glassy carbon substrate. All surfaces were Ar-ion etched for 45 s prior to data collection.

All surfaces were Ar-ion etched for 45 s prior to XPS analysis to remove absorbed water, carbon dioxide, and adventitious carbon compounds. Pt $4f_{7/2}$ peaks were observed at ~ 71.2 eV for both the ALD and e-beam evaporated Pt samples, while no peaks were observed for PtO (or Pt(OH)₂)

and PtO₂, which are shifted by ~1.2 and ~3 eV, respectively, relative to Pt metal (Figure 4) [29].

XPS depth profiling showed metallic Pt composition throughout the ALD film (Figure 5).

Figure 5. XPS showing the Pt 4f_{7/2} region for ALD (50 cycles, 250 °C) Pt films on a glassy carbon substrate a) after Ar-ion etching for 45 s, b) the same sample after an additional 45 s of argon-ion etching.

No carbon signal was detected on the ALD-grown Pt sample (Figure 6) implying that after the initial ion etching the Pt film contained only very small amounts of residual ligand from the

MeCpPtMe₃ precursor and that the Pt film completely covered the carbon surface. The ALD Pt precursor, MeCpPtMe₃ and Pt salts have binding energies at ≥ 72.5 eV, and no evidence of these materials was detected in the XP spectra of the samples [30]. The position of the Pt 4f_{7/2} peaks was independent of the deposition temperature for 200 or 300 °C .

Figure 6. XPS showing the C 1s region of ALD (50 cycles at 250 °C) Pt films on glassy carbon substrates after (a) one or (b) two cycles of 45 s of Ar-ion etching. The carbon 1s signal was observed only after the second etching cycle.

Similarly, results were observed for 50 cycles of ALD Pt films deposited on Si. No Pt oxide or carbon was observed after the initial ion etching pretreatment and only Pt metal was observed with further etching.

C. Catalytic activity for the HER

Figure 7 shows the representative rotating disk voltammograms in 1 M H₂SO₄(aq) saturated with H₂ gas, for Pt films deposited by electron-beam evaporation and by ALD onto glassy carbon substrates. Figure 7 shows the electrochemical performance of Pt films deposited by ALD or by electron-beam evaporation. Pt films of 3 nm thickness prepared on glassy carbon electrodes using either ALD or electron-beam evaporation exhibited similar electrochemical behavior and required overpotentials of -33.6 ± 0.4 mV and 33.3 ± 0.8 mV ($E^{H^+/H_2}(1M H_2SO_4) = -241$ mV vs SCE), respectively to achieve a current density of 10 mA cm^{-2} (geometric surface area) and were within experimental error of each other.

Figure 7. Electrochemical performance of glassy carbon-disk electrodes with 3 nm of Pt deposited by ALD and by electron-beam evaporation in a H₂-saturated 1.0 M H₂SO₄ solution. The disk electrodes were rotated at a rate of 1600 rpm, and the scan rate was 50 mV/s.

Discussion

The growth rate (110 pm/cycle) of the Pt films (calculated after the initial 50 cycles) achieved using the ALD method described herein is significantly greater than that observed either for use of $\text{Pt}(\text{acac})_2$ (50 pm/cycle) or MeCpPtMe_3 and oxygen (10–50 pm/cycle).[17-22] In addition, some of the growth rates for ALD of Pt were calculated based on NPs [17-19], and thus represents significantly less deposition than the continuous films grown in this work. The principal synthetic difference between the method described herein and most previously reported methods is the use of the stronger oxidant ozone rather than oxygen.

During the ALD process, the ligands on the MeCpPtMe_3 complex were removed during the ozone cycle, likely leaving PtOx on the surface. The PtOx would then be reduced to metallic Pt on the subsequent step by the departing ligands of the Pt precursor as recently reported for similar systems [23, 24, 31, 32]. The ALD grown Pt in this work was shown to be metallic below the surface layer by XPS depth profile analysis (Figure 4).

Optimal growth conditions were achieved using a chamber temperature of 250 °C, and a MeCpPtMe_3 exposure duration of 1.0 s (4 pulses of 0.25 s each) followed by an ozone exposure of 0.1 s for each cycle. These conditions yielded continuous thin films of Pt with consistent growth rates for up to 500 cycles (the greatest number of cycles used for this work). Recent reports by S. F. Bent's and J. Denooven's groups of ALD Pt grown using MeCpPtMe_3 and ozone gave growth rates that differ from those reported herein. Bent's group [25] reported growth rates that varied from 25 to 70 pm/cycle for temperatures of 100 to 400 °C in a custom-made "showerhead" design ALD system. The growth rates decreased significantly for temperature below 200 °C. J. Dendooven's group [26] reported Pt growth rates of about 45 pm/cycle for

temperatures 100 to 300 °C using a cold wall ALD system. These variations show the sensitivity of growth rates to ALD system design, heating source, and the ozone concentrations.

The increased rate of Pt deposition at temperatures lower than those used for other high rate deposition methods, and without the need for the plasma treatments of thermal ALD processes [33], should reduce the corrosion or oxidation of substrates that can occur during deposition. Moreover, the ability to deposit a continuous catalyst film that completely covers a substrate could allow photoelectrode materials that are unstable under water-splitting conditions to be protected against electrochemical corrosion by preventing direct physical contact between the unstable semiconductor and the electrolyte.

The temperature window of 200 – 300 °C provides advantages for other applications, such as the fabrication of patterned electrodes and other applications that require compatibility with other materials. For example, the polymer mask material SU-8, commonly used for photolithography, undergoes glass transitions at temperatures above 200 °C, and therefore an ALD process that allows a catalyst to be deposited at a temperature lower than 200 °C would be useful in the fabrication of well patterned catalyst/semiconductor heterojunctions for photoelectrochemical applications. Compared with other deposition methods, ALD gives well-controlled deposition, and is a facile process that requires relatively low temperatures and that has potential for use in large-scale fabrication of materials.

Conclusion

ALD was used to grow Pt nanoparticles and thin films of Pt NPs under varied growth conditions. Using the precursors MeCpPtMe₃ and ozone and temperatures as low as 200 °C, a growth rate of 110 pm/cycle was achieved after 50 cycles of inhibition time. AFM and SEM showed that the Pt

films grown using the ALD method were uniform over the surface of the sample, and XPS characterization confirmed the composition of the films as metallic Pt. The electrocatalytic activity of ALD Pt films grown on glassy carbon electrodes showed identical activity for the hydrogen-evolution reaction, within experimental error, to that of films deposited using electron-beam evaporation. The low temperatures and decreased processing time required to produce uniform films of Pt with high catalytic activity for the HER using this ALD method may impact many applications, particularly those that require simultaneous processing of multiple materials and/or well-controlled interfaces.

AUTHOR INFORMATION

Corresponding Author

* Email: bsb@caltech.edu,

* Email: nslewis@caltech.edu

ACKNOWLEDGMENTS

This work was supported by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department of Energy under Award Number DE-SC0004993. BSB was supported by the Beckmann Institute of California Institute of Technology. Research was in part carried out at the Molecular Materials Research Center of the Beckman Institute of the California Institute of Technology. LH would like to thank the VIDI project granted to Dr. Arno H.M. Smets by NWO-STW to financially support his stay in California Institute of Technology.

REFERENCES

- [1] I. Oh, J. Kye, S. Hwang, Enhanced Photoelectrochemical Hydrogen Production from Silicon Nanowire Array Photocathode, *Nano Lett.* 12 (2012) 298-302.
- [2] S.Y. Reece, J.A. Hamel, K. Sung, T.D. Jarvi, A.J. Esswein, J.J.H. Pijpers, D.G. Nocera, Wireless Solar Water Splitting Using Silicon-Based Semiconductors and Earth-Abundant Catalysts, *Science* 334 (2011) 645-648.
- [3] J.R. McKone, A.P. Pieterick, H.B. Gray, N.S. Lewis, Hydrogen Evolution from Pt/Ru-Coated p-Type WSe₂ Photocathodes, *J. Am. Chem. Soc.* 135 (2013) 223-231.
- [4] J.R.M. Zhuangqun Huang, Chengxiang Xiang, Ronald L. Grimm, Emily L. Warren, Joshua M. Spurgeon, Hans-Joachim Lewerenz, Bruce S. Brunshawig, Nathan S. Lewis, Comparison between the measured and modeled hydrogen-evolution activity of Ni- or Pt-coated silicon photocathodes, *Int.J. Hydrogen Energy* 39 (2014) 16220–16226.
- [5] J.R. McKone, E.L. Warren, M.J. Bierman, S.W. Boettcher, B.S. Brunshawig, N.S. Lewis, H.B. Gray, Evaluation of Pt, Ni, and Ni-Mo electrocatalysts for hydrogen evolution on crystalline Si electrodes, *Energy Environ. Sci.* 4 (2011) 3573-3583.
- [6] J.O. Bockris, I.A. Ammar, A. Huq, The mechanism of the hydrogen evolution reaction on platinum, silver, and tungsten surfaces in acid solutions., *J. Phys. Chem.* 61 (1957) 879-886.
- [7] A. Caillard, P. Brault, J. Mathias, C. Charles, R.W. Boswell, T. Sauvage, Deposition and diffusion of platinum nanoparticles in porous carbon assisted by plasma sputtering, *Surf. Coat. Technol.* 200 (2005) 391-394.
- [8] X.M. Yan, S. Kwon, A.M. Contreras, J. Bokor, G.A. Somorjai, Fabrication of large number density platinum nanowire arrays by size reduction lithography and nanoimprint lithography, *Nano Lett.* 5 (2005) 745-748.

- [9] J.R.V. Garcia, T. Goto, Chemical vapor deposition of iridium, platinum, rhodium and palladium, *Mater Tran.*, 44 (2003) 1717-1728.
- [10] Y.L. Rui Liu, Lien-Yang Chou, Stafford W. Sheehan, Wenshu He, Fan Zhang, Harvey J. M. Hou, Dunwei Wang, Water Splitting Using Tungsten Oxide Prepared by Atomic Layer Deposition and Stabilized by Oxygen-Evolving Catalyst, *Angew. Chem. Int. Ed.* 50 (2011) 499-502.
- [11] L.Y. Chou, R. Liu, W.S. He, N. Geh, Y.J. Lin, E.Y.F. Hou, D.W. Wang, H.J.M. Hou, Direct oxygen and hydrogen production by photo water splitting using a robust bioinspired manganese-oxo oligomer complex/tungsten oxide catalytic system, *Int. J. Hydrogen Energy* 37 (2012) 8889-8896.
- [12] X.G. Yang, C. Du, R. Liu, J. Xie, D.W. Wang, Balancing photovoltage generation and charge-transfer enhancement for catalyst-decorated photoelectrochemical water splitting: A case study of the hematite/MnOx combination, *J. Catal.* 304 (2013) 86-91.
- [13] M.H. Lee, K. Takei, J.J. Zhang, R. Kapadia, M. Zheng, Y.Z. Chen, J. Nah, T.S. Matthews, Y.L. Chueh, J.W. Ager, A. Javey, p-Type InP Nanopillar Photocathodes for Efficient Solar-Driven Hydrogen Production, *Angew Chem. Int. Ed.* 51 (2012) 10760-10764.
- [14] Y.W. Chen, J.D. Prange, S. Duhnen, Y. Park, M. Gunji, C.E.D. Chidsey, P.C. McIntyre, Atomic layer-deposited tunnel oxide stabilizes silicon photoanodes for water oxidation, *Nat. Mater.* 10 (2011) 539-544.
- [15] M.F. Lichterman, M.R. Shaner, S.G. Handler, B.S. Brunschwig, H.B. Gray, N.S. Lewis, J.M. Spurgeon, Enhanced Stability and Activity for Water Oxidation in Alkaline Media with Bismuth Vanadate Photoelectrodes Modified with a Cobalt Oxide Catalytic Layer Produced by Atomic Layer Deposition, *J. Phys. Chem. Lett.* 4 (2013) 4188-4191.

- [16] N.C. Strandwitz, D.J. Comstock, R.L. Grimm, A.C. Nichols-Nieler, J. Elam, N.S. Lewis, Photoelectrochemical Behavior of n-type Si(100) Electrodes Coated with Thin Films of Manganese Oxide Grown by Atomic Layer Deposition, *J. Phys. Chem. C* 117 (2013) 4931-4936.
- [17] C.L. Neil P. Dasgupta, Sean Andrews, Fritz B. Prinz, and Peidong Yang, Atomic Layer Deposition of Platinum Catalysts on Nanowire Surfaces for Photoelectrochemical Water Reduction, *J. Am. Chem. Soc.* 135 (2013) 12932–12935.
- [18] P. Dai, J. Xie, M.T. Mayer, X. Yang, J. Zhan, D. Wang, Solar Hydrogen Generation by Silicon Nanowires Modified with Platinum Nanoparticle Catalysts by Atomic Layer Deposition, *Angew. Chem.Int. Ed.* 52 (2013) 11119-11123.
- [19] A.J.M.M. Matthieu J. Weber, Marcel A. Verheijen, Cees van der Marel, and Wilhelmus M. M. Kessels, Supported Core/Shell Bimetallic Nanoparticles Synthesis by Atomic Layer Deposition, *Chem. Mater.* 24 (2012) 2973–2977.
- [20] N.L. Adriaan J. M. Mackus, Layton Baker, and Wilhelmus M. M. Kessels, Catalytic Combustion and Dehydrogenation Reactions during Atomic Layer Deposition of Platinum, *Chem. Mater.* 24 (2012) 1752–1761.
- [21] J. Hamalainen, F. Munnik, M. Ritala, M. Leskela, Atomic Layer Deposition of Platinum Oxide and Metallic Platinum Thin Films from Pt(acac)₂ and Ozone, *Chem. Mater.* 20 (2008) 6840-6846.
- [22] T. Aaltonen, M. Ritala, T. Sajavaara, J. Keinonen, M. Leskela, Atomic layer deposition of platinum thin films, *Chem. Mater.* 15 (2003) 1924-1928.
- [23] J. Hamalainen, E. Puukilainen, T. Sajavaara, M. Ritala, M. Leskela, Low temperature atomic layer deposition of noble metals using ozone and molecular hydrogen as reactants, *Thin Solid Films* 531 (2013) 243-250.

- [24] J. Hamalainen, M. Ritala, M. Leskela, Atomic Layer Deposition of Noble Metals and Their Oxides, *Chem. Mater.* 26 (2014) 786-801.
- [25] H.-B.-R. Lee, K.L. Pickrahn, S.F. Bent, Effect of O₃ on Growth of Pt by Atomic Layer Deposition, *J. Phys. Chem. C* 118 (2014) 12325-12332.
- [26] J. Dendooven, R. K. Ramachandran, K. Devloo-Casier, G. Rampelberg, M. Filez, H. Poelman, G. B. Marin, E. Fonda, and C. Detavernier, L. Baker, A. S. Cavanagh, D. Seghete, S. M. George, A. J. M. Mackus, W. M. M. Kessels, Z. Y. Liu, and F. T. Wagner, Low-Temperature Atomic Layer Deposition of Platinum Using (Methylcyclopentadienyl)trimethylplatinum and Ozone, *J. Phys. Chem. C* 117 (2013) 20557–20561.
- [27] C.E.D.C. Christopher P. Wade, Etch-pit initiation by dissolved oxygen on terraces of H-Si(111), *Appl. Phys. Lett.* 71 (1997) 1679.
- [28] H.B.R. Lee, S.H. Baeck, T.F. Jaramillo, S.F. Bent, Growth of Pt Nanowires by Atomic Layer Deposition on Highly Ordered Pyrolytic Graphite, *Nano Lett.* 13 (2013) 457-463.
- [29] K. Qadir, S.H. Kim, S.M. Kim, H. Ha, J.Y. Park, Support Effect of Arc Plasma Deposited Pt Nanoparticles/TiO₂ Substrate on Catalytic Activity of CO Oxidation, *J. Phys. Chem. C* 116 (2012) 24054-24059.
- [30] C. Battistoni, A.M. Giuliani, E. Paparazzo, F. Tarli, Platinum Complexes of the Methyl-Esters of Dithiocarbazic Acid and 3-Phenyldithiocarbazic Acid, *J Chem Soc Dalton*, (1984) 1293-1299.
- [31] W.M.M. Kessels, H.C.M. Knoops, S.A.F. Dielissen, A.J.M. Mackus, M.C.M. van de Sanden, Surface reactions during atomic layer deposition of Pt derived from gas phase infrared spectroscopy, *Appl. Phys. Lett.* 95 (2009) 013114.

- [32] W. Setthapun, W.D. Williams, S.M. Kim, H. Feng, J.W. Elam, F.A. Rabuffetti, K.R. Poepelmeier, P.C. Stair, E.A. Stach, F.H. Ribeiro, J.T. Miller, C.L. Marshall, Genesis and Evolution of Surface Species during Pt Atomic Layer Deposition on Oxide Supports Characterized by in Situ XAFS Analysis and Water-Gas Shift Reaction, *J. Phys. Chem. C* 114 (2010) 9758-9771.
- [33] L. Baker, A.S. Cavanagh, D. Seghete, S.M. George, A.J.M. Mackus, W.M.M. Kessels, Z.Y. Liu, F.T. Wagner, Nucleation and growth of Pt atomic layer deposition on Al_2O_3 substrates using (methylcyclopentadienyl)-trimethyl platinum and O_2 plasma, *J. Appl. Phys.* 109 (2011) 084333.