

The process of molecular plating and the characteristics of the produced thin films – What we have learned in 60 years and what is still unknown

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Abstract. Molecular plating is a well-established and widely used method for producing thin films of various elements, which are used in variety of nuclear physics applications. Sixty years have passed since the method was established, and some insights into the chemical process underlying the method and the composition of the thin films have been gained. A brief overview of what has been learned about molecular plating since its introduction and the methods applied in the characterization of molecular plated thin films is given here. Through various spectroscopic and microscopic methods, the process of molecular plating and the chemical composition are gradually being elucidated, albeit we still do not understand all aspects.

1 Introduction

The molecular plating (MP) method for the production of mechanically stable thin films of radioisotopes was introduced by Parker and Falk in 1962 [1]. In this method, a salt of the respective element was dissolved in a small volume of diluted acids, added to an organic solution, e.g., alcohols or acetone and then electrochemically deposited. Nowadays, a constant current density of $<1 \text{ mA/cm}^2$ over 1-2 h is applied. This results in high voltages of several hundred volts. MP produces uniform thin films with an even distribution of the deposited element. Such layers found widespread applications, e.g., as targets in ion beam experiments, as recoil sources, or as α -particle sources [3-12]. One example is the synthesis of superheavy elements (SHE), which can be produced in the nuclear fusion of a light projectile with a heavy target nuclide. All known isotopes of the elements with atomic number $Z \geq 113$ resulted from actinide-target based reactions [11]. Typical isotopes like ^{244}Pu , ^{248}Cm or ^{249}Bk are only available in small quantities, rendering production methods with high yields necessary. Therefore, MP has become the standard method for producing these targets [3,11,12]. For this application, the method works reliable up to film thicknesses of $\approx 800 \mu\text{g/cm}^2$, with yields of usually over 90 % [2,3,4]. While thicker films can be produced for various elements, the method becomes unreliable for actinide layers. Consequently, actinide films that are substantially thicker have not been reported. Although molecular plating was introduced in 1962 [1] and has been widely used since, neither the mechanism of the deposition process, nor the

exact composition of the resulting thin layer is fully understood. Parker and Falk coined the method “molecular plating” because they assumed at the time that the provided salts, e.g., the nitrates or chlorides, would be deposited as thin films [1]. Nowadays, it is well known that this is not the case. Many different analytical methods [2,12-18] have shown that the chemical species of the deposited element in the thin film differs from the species in the solution. Over time, mostly microscopic and also some spectroscopic methods have been used to analyse the thin films produced by MP and to understand how the process works, see e.g., [2,4,18,19]. The elucidation of the process and the layer properties appear necessary to produce improved films, which e.g., exceed the limitations in the layer thicknesses, as it appears desirable for, e.g., SHE production [4].

2 Methods

Many methods focused on the film’s morphology, which led to the use of several microscopic methods, such as scanning electron microscopy (SEM) [6,17,21,22] and atomic force microscopy (AFM) [2,16,17]. Radiographic imaging (RI) [18,23,24] exploits the radioactive character of actinides to provide information on the spatial distribution of the radioisotope. Alpha and gamma spectroscopy [8,9,21,23,24] provide further quantitative information.

Neutron activation analysis (NAA) [25] can be used to activate inactive samples or long-lived isotopes,

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making gamma measurements possible that reveal the amount of deposited material.

With SEM, energy-dispersive X-ray spectroscopy (EDS) was also employed early on to determine the elemental composition of the thin films. [13,15,19,26]. However, these methods are all unable to provide information on the chemical composition of the thin films, which is why spectroscopic methods, like IR, Raman, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), or ion beam spectroscopy like elastic recoil detection analysis (ERDA), Rutherford backscattering (RBS) or proton-induced X-ray emission (PIXE), were also used later [2,13,15,16,19,27-29].

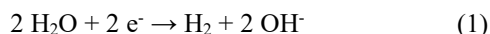
Raman and IR measurements were made early on [15,19], but not recently pursued further. These methods allow determining the chemical composition. Both methods are complementary as the vibrations of the molecules are either IR or Raman active. Further information can be gained by XPS [2,16,17], which provides information on the chemical environment of the element. XRD measurements were used to investigate the crystalline composition of the films [13,14] to reach conclusions about the crystalline structure.

Most recently, various ion beam analyses have also been applied to molecular plated thin films. One such method is ERDA [4], which is particularly well suited for detecting light elements from lithium up to chlorine in the thin film. Complementary to this, RBS was also used [12,28,29] to allow drawing conclusions about the elemental composition of the films.

PIXE was also measured in combination with RBS [4]. In PIXE, a proton beam induces X-rays in the sample to obtain further information about the film. It can also be used as an imaging method, which allows both microscopic and spectroscopic information to be obtained simultaneously.

3 Elucidation of the MP process

In 1959, even before MP was introduced, Hansen [30] had published a theory on electrochemical deposition from water or mixtures of water with alcohols or acetone. He suggested that water is reduced in the process, producing hydroxide ions that lead to basic precipitation of the actinides [19,30]:



In 1975, Ramaniah et al. [15] were able to determine through thermogravimetric, EDS and IR analyses that no nitrates were present in MP films. In particular, the IR analyses of uranium films showed a U-O stretching vibration of UO_2^{2+} , which led to the assumption that uranium was deposited as an oxide or hydroxide. In addition, by adding phenolphthalein, the presence of water was observed in the isopropyl alcoholic solution and a hydroxide-rich layer was observed at the cathode [15]. Sadi et al. [19] proposed the chemical composition to be $\text{UO}_2(\text{OH})_2$, based on the atomic ratios determined by EDS measurements. They proposed the hydroxide ions to act as bridge ligands between the uranyl ions as

a possible structure in the thin film. With more analytical investigations, it became clear that the MP process is even more complex than a hydroxide precipitation, and the thin films contain more than only oxide and hydroxide species [2,14-17,19,27].

4 Elucidation of the properties of MP films

With the help of microscopic methods, the thin layers could be examined in detail. Since the focus was particularly on the deposition of uranium and plutonium in the beginning, the activity of these elements was used to take radiographic images of the samples [18]. These images showed that the activity of the films was particularly homogeneously distributed, which is visible in Fig. 1.

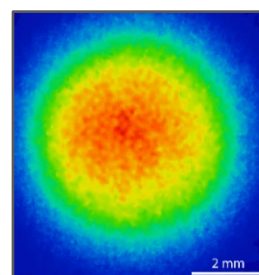


Fig. 1. A radiographic image (RI) of a terbium thin film, produced by MP, with a layer thickness of 500(50) $\mu\text{g}/\text{cm}^2$. Natural terbium was neutron activated in the TRIGA Mainz research reactor [25] before plating.

Radiographic images also made it possible to identify the influence of various experimental parameters, such as cell design or electrode shape, on the deposition. In this way, information could be obtained about the influence of the geometry of the anode, i.e., the counter-electrode, on the distribution of the activity in the thin film [23,24,31,32]. Initial experiments also show that stirring with a rotating anode or an ultrasonic stirrer during deposition can lead to shorter deposition times by forcing convection in the solution. However, the choice of parameters is crucial [7,23,24]. Due to the activity of uranium and thorium isotopes, alpha and gamma spectra of samples produced by molecular plating could also be taken, so that the deposition yield could be optimized by adjusting the deposition time and the applied current [1-3,18-23,31,32].

The usage of a SEM with a spatial resolution of $<1 \mu\text{m}$ [4] made it clear that the molecular plated thin films were not homogeneous and closed surfaces as was inferred from radiographic images, which have a spatial resolution of $>100 \mu\text{m}$ [33], but consisted of many cracks and tiles, referred to as “mudcracking” [1,4,20,26,27]. Pictures of such tiles are visible in Fig. 2. Today, SEM measurements are a standard method to characterise molecular-plated thin films in higher resolution than a usual light microscope [4,16,18,21].

Later Liebe et al. [13] confirmed the absence of nitrogen, as first reported by Ramaniah et al. [15], in the thin MP films by EDS measurements. Therefore, nitrates cannot be present in the thin films, which

definitely refuted Parker and Falk's theory of salt re-deposition [1].

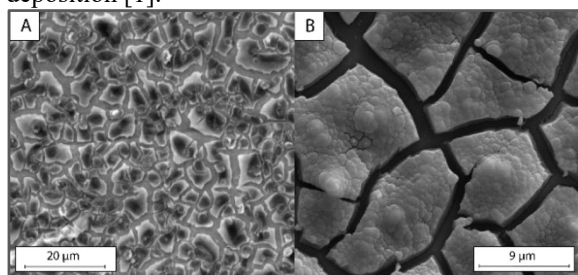


Fig 2. SEM pictures of lanthanide thin films produced by molecular plating. A) Erbium thin film. B) Silver sputtered lanthanum thin film. Both thin films have a layer thickness of 500(50) $\mu\text{g}/\text{cm}^2$.

Vascon et al. [16] were able to show by AFM measurements in solution that cracks are not present in the native film during the MP process, but form only after removal of the solvent, during drying after deposition. Fig. 3 shows an exemplary AFM image of a Tb thin film, after the drying process. They could also show that different solvents impact the quality of the thin film [16] and explained this by the fact that different solvents have different boiling points and different vapour pressures. It is assumed that residues of the solvents are present in the film after deposition. Evaporation during drying leads to rupturing of the films. They were able to observe that deposition from DMF (boiling point: 153 °C), leads to less mudcracking than deposition from isobutanol (boiling point: 108 °C).

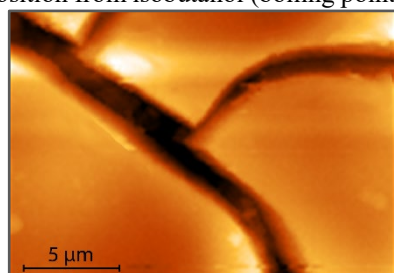


Fig 3. An AFM picture of a terbium thin film with a layer thickness of 100(10) $\mu\text{g}/\text{cm}^2$, which was produced by molecular plating.

Vascon et al. [2,16,17] also found out with the help of XPS measurements that the produced thin films not only contained oxides and hydroxides, but also organic components. Besides adventitious carbon contamination, aliphatic and aromatic carbon was found [2,16,17]. It did not disappear even after sputtering with 4 kV Ar^+ -ions for 10 min. They thus assumed that the carbon was a constituent of the thin film. They attributed the signals to the presence of residue solvents, carbonates and/or carboxylates, which was assumed to form by the electrolysis of the used solvents. Further XPS measurements also showed that the lanthanide is not reduced in the process of plating but remains in the +III oxidation state [2,13,15-17].

In 2016, Choi and Chung [13] did XRD measurements on molecular-plated thin films to understand what happens to the thin films when they are calcinated. They identified, next to oxides and hydroxides, also predominantly oxycarbonates after a short calcination time, further proving that significant

amounts of organic molecules were present in the molecular plated thin films.

Mayorov et al. [26] investigated Gd MP thin films after irradiation with ion beams ($^{48}\text{Ca}^{7+}$ with 3.8 MeV/u and 4.5×10^{14} ions/ cm^2 and $^{45}\text{Sc}^{6+}$ with 4.7 MeV/u and 4.0×10^{15} ions/ cm^2). In the XRD measurements, the only visible compound before and after the irradiation was Gd_2O_3 . The EDS spectra showed, in addition to gadolinium, also carbon which they attributed to carboxylates because of this prior assignment by Vascon et al. [2,16,17]. Mayorov et al. assumed that organic residues evaporated during the irradiation leading to a decreased carbon signal. The SEM picture showed that the typical cracked film became smoother and thinner after the irradiation, closing the cracks, which were visible before [26].

Although much has been learned about the MP method and the produced thin films, much is still unknown. It is not still clear why high voltages of several hundred volts are necessary for this method to work sufficiently well. It is also unknown what happens to most of the current that is applied during the MP process, and whether this loss of charge has any influence [2]. It is also unknown why the layer thickness is limited to 800 $\mu\text{g}/\text{cm}^2$ and how this limit can be exceeded [3,4]. Although individual components such as oxides, hydroxides, carbonates, and carboxylates have been identified in the thin films [2,7,12-17,19,27], the ratios of the individual components to each other are still unknown. It is therefore not yet possible to determine a sum formula for the composition of the film.

5 Conclusion

Since the establishment of molecular plating by Parker and Falk [1] 60 years ago, knowledge about the method has been gained via many different methods. Via different microscopic methods, like RI, SEM and AFM, and different spectroscopic methods, like alpha and gamma spectroscopy, EDS, XPS, XRD, RBS, IR, and Raman spectroscopy [2,4,7,13-17,19,27], a more precise understanding of the process of MP and of the chemical composition of the thin films was obtained.

It became clear that no nitrates or chlorides are deposited, but that the thin film consisted mainly of oxides and hydroxides. In addition, carboxylates and carbonates are also present [2,16,17]. It was also shown that the choice of solvent during deposition has an influence on the film quality [16].

By exposing MP films to heavy ion beams, they are further modified, making them thinner and closing the cracks [26].

We still do not fully know, what the stoichiometric composition of MP films is and what influences the success or failure of a deposition [4,16,21,22]. In addition, it is still not understood, why the thicknesses of the produced thin films are limited and how to overcome this obstacle [3,4].

Therefore, further studies of the MP process and of the resulting layers are necessary, alongside further development to improve the method for future applications. In this way, further systematic studies

could be carried out to understand the influence of CO₂ and water on the MP process.

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References

1. W. Parker, R. Falk, Nucl. Instr. And Meth. **16**, 355-357 (1962)
2. A. Vascon, S. Santi, A. A. Isse, T. Reich, J. Drebert, H. Christ, Ch. E. Düllmann, K. Eberhardt, Nucl. Instrum. Methods. Phys. Res. A, **696**, 163-175 (2012)
3. K. Eberhardt, W. Brüchle, Ch. E. Düllmann, K. E. Gregorich, W. Hartmann, A. Hübner, E. Jäger, B. Kindler, J. V. Kratz, D. Liebe, B. Lommel, H.-J. Maier, M. Schädel, B. Schausten, E. Schimpf, A. Semchenkov, J. Steiner, J. Szerypo, P. Thörle, A. Türler, A. Yakushev, Nucl. Instrum. Methods. Phys. Res. A, **590**, 134-140 (2008)
4. Ch. E. Düllmann, E. Artes, A. Dragoun, R. Haas, E. Jäger, B. Kindler, B. Lommel, K.-M. Mangold, C.-C. Meyer, C. Mokry, F. Munnik, M. Rapps, D. Renisch, J. Runke, A. Seibert, M. Stöckl, P. Thörle-Pospiech, C. Trautmann, N. Trautmann, A. Yakushev, J. Radioanal. Nucl. Chem. (2022) <https://doi.org/10.1007/s10967-022-08631-4>
5. J. Runke, Ch. E. Düllmann, K. Eberhardt, P. A. Ellison, K. E. Gregorich, S. Hofmann, E. Jäger, B. Kindler, J. V. Kratz, J. Krier, B. Lommel, C. Mokry, H. Nitsche, J. B. Roberto, K. P. Rykaczewski, M. Schädel, P. Thörle-Pospiech, N. Trautmann, A. Yakushev, J. Radioanal. Nucl. Chem. **299**, 1081-1084 (2014)
6. B. Lommel, Ch. E. Düllmann, B. Kindler, D. Renisch, Eur. Phys. J. A, (accepted for publication)
7. W. Loveland, J. D. Baker, J. Radioanal. Nucl. Chem **282**, 361-363 (2009)
8. W. Loveland J. Radioanal. Nucl. Chem **307**, 1591-1594 (2016)
9. A. Vascon, Ch. E. Düllmann, K. Eberhardt, B. Kindler, B. Lommel, J. Runke, Nucl. Instrum. Methods. Phys. Res. A **655**, 72-79 (2011)
10. J. P. Greene, R. V. F. Janssens, I. Ahmad, Nucl. Instrum. Methods. Phys. Res. A **438**, 119-123 (1999)
11. R. Haas, T. Kieck, D. Budker, Ch. E. Düllmann, K. Groot-Berning, W. Li, D. Renisch, F. Schmidt-Kaler, F. Stopp, A. Viatkina, Hyperfine Interactions **241**, 25 (2020)
12. R. Haas, M. Hufnagel, R. Abrosimov, Ch. E. Düllmann, D. Krupp, C. Mokry, D. Renisch, J. Runke, U. W. Scherer, Radiochim. Acta **108**, 923-941 (2018)
13. D. Liebe, K. Eberhardt, W. Hartmann, T. Häger, A. Hübner, J. V. Kratz, B. Kindler, B. Lommel, p. Thörle, J. Steiner, Nucl. Instrum. Methods. Phys. Res. A, **590**, 145-150 (2008)
14. J. Choi, Y. H. Chung, Journal of Nanomaterials, **2016**, 5140219 (2016)
15. M. V. Ramaniah, R. J. Singh, S. K. Awasthi, S. Prakash, Int J Appl Radiat Isot **26**, 648-650 (1975)
16. A. Vascon, S. Santi, A. A. Isse, A. Kühnle, T. Reich, J. Drebert, K. Eberhardt, Ch. E. Düllmann Nucl. Instrum. Methods Phys. Res. A **714**, 163-175 (2013)
17. A. Vascon, J. Runke, N. Trautmann, B. Cremer, K. Eberhardt, Ch. E. Düllmann, Appl. Radiat. Isot. **95**, 36-43 (2015)
18. N. Getoff, H. Bildstein, Nucl. Instr. And Meth. **36**, 173-175 (1965)
19. S. Sadi, A. Paulenova, P. R. Watson, W. Loveland, Nucl. Instrum. Methods. Phys. Res. A, **655**, 80-84 (2011)
20. Ch. E. Düllmann, M. Block, F. P. Heßberger, J. Khuyagbaatar, B. Kindler, J. V. Kratz, B. Lommel, G. Münzenberg, V. Pershina, D. Renisch, M. Schädel, A. Yakushev, Radiochim. Acta, **110**, 417-439 (2022)
21. W. Parker, H. Bildstein, N. Getoff, Nucl. Instr. And Meth. **26**, 55-60 (1964)
22. W. Parker, H. Bildstein, N. Getoff, H. Fischer-Colbrie, H. Regal, Nucl. Instr. And Meth. **26**, 61-65 (1963)
23. M. T. Crespo, Appl. Radiat. Isot. **70**, 210-215 (2012)
24. H. Klemenčič, L. Benedik, Appl. Radiat. Isot. **68**, 1247-1251 (2010)
25. K. Eberhardt, C. Geppert, Radiochim. Acta **107**, 535-546 (2019)
26. D. A. Mayorov, E. E. Tereshatov, T. A. Werke, M. M. Frey, C. M. Folden III, Nucl. Instrum. Methods. Phys. Res. B **407**, 256-264 (2017)
27. C.-C. Meyer, A. Dragoun, Ch. E. Düllmann, R. Haas, E. Jäger, B. Kindler, B. Lommel, A. Prosvetov, M. Rapps, D. Renisch, P. Simon, M. Tomut, C. Trautmann, A. Yakushev, Nucl. Instrum. Methods. Phys. Res. A, **1028**, 166365 (2022)
28. O. A. Wasson, R. A. Schrack, Nucl. Instrum. Methods. Phys. Res. A **282**, 194-198 (1989)
29. C. Stodel, EPJ Web of Conferences **229**, 02001 (2020)
30. P. G. Hansen, J. Inorg. Nucl. Chem. **12**, 30-37 (1959)
31. Young Gun Ko, J. Radioanal. Nucl. Chem. **326**, 861-877 (2020)
32. C. Ingelbrecht, A. Moens, R. Eykens, A. Dean, Nucl. Instrum. Methods. Phys. Res. A, **397**, 34-38 (1997)
33. R. Haas, L. Lohse, Ch. E. Düllmann, K. Eberhardt, C. Mokry, J. Runke, Nucl. Instrum. Methods. Phys. Res. A, **874**, 43-49(2017)