中国科学院
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Uranium Targets Prepared by Pulse Molecular Plating and Target Characterization

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Outline

1. Introdution and motivation
2. Uranium targets preparation by pulse molecular plating
- Pulse plating parameters optimization by orthogonal test
- Targets homogeneity investigations
3. Th targets preparation on 2μm-thick Al foil and Nd, Gd on 2μm-thick Ti foil
4. Summary

The heaviest elements are synthesized in heavy-ion induced hot fusion reactions with various actinide targets. Because the actinide material is often available only in very limited amounts, such as ^{242,244}Pu, ^{243}Am, ^{248}Cm, ^{249}Bk, and ^{249}Cf,the deposition method with high yields (~90 %) is required.

The molecular plating method had been widely used for decades to prepare actinides targets (Trautmann et al., 1982; Evans et al., 1972;Mullen and Aumann, 1975; Aumann and Muller, 1974).

Types of methods for preparation of actinides targets in ORNL

- ✓ High yields （approaching 100%）
- ✓ Simple device and preparation procedure
- ✓ Good adherence （< 100 μg/cm²）
- ✓ Acceptable uniformity

Table 3
Types of methods used in preparation of actinide targets

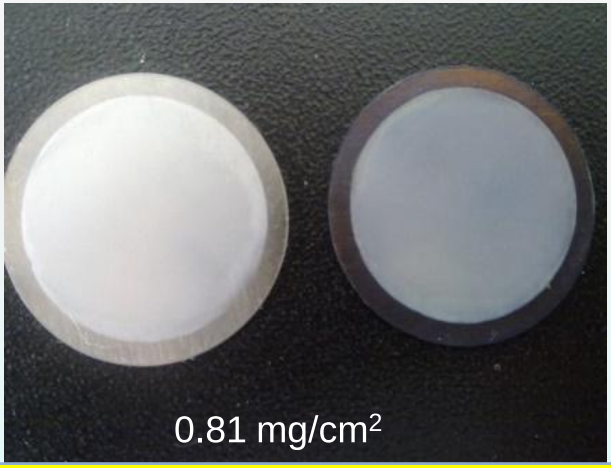
Element	Range of thickness (μg/cm²)	Method of preparation[b]	Backing[a]	Form of deposit
Am	< 1 to 5000[c]	1	Al, Pt, Ti	AmO_2
	10000 up	1,2,4	Self-supported	Am
Cm	< 1 to 5000[c]	1	Al, Ti, C	Cm_2O_3, CmF_3
	15000 up	1,2	Self-supported	
Cf	≪ 1 to 10	1	Pt, Ni, C, Au	Oxychloride
	≪ 1 to 1	5	Pt, Ni, C, Au	Oxychloride
	≪ 1 to 1	6	Pt, Ni	Oxychloride
Np	< 1 to 12000[c]	1	Al, Ti	NpO_2
Pu	< 1 to 5000[c]	1	Al, Ti, Pt	PuO_2
	15000 up	1,2,4	Self-supported	Pu
U	< 1 to 12000[c]	1	Al, Ti, Ni, Pt	UO_2
	15000 up	3,4	Self-supported	

Untill now，The relatively thick targets preparation by MP remains an unresolved issue.

Motivation

In reaction ^{173}Yb *(p,n)* ^{173}Lu *, thick Yb targets were produced by* multiple deposition with direct current plating

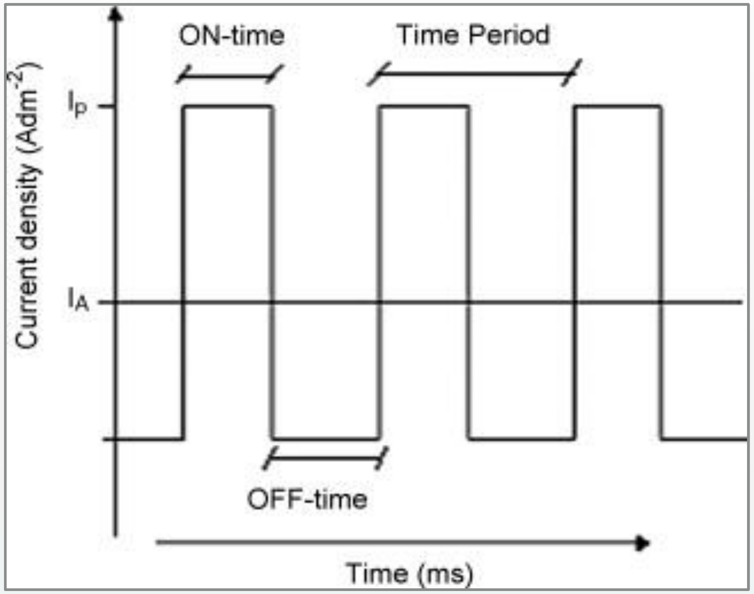
Deposition steps	Yb（mg）	Yield (%)	Yb（mg）	Yields(%)
1	1.49	94.80	1.57	89.54
2	2.50	84.26	2.68	87.64
3	/	/	1.99	93.35
Thickness（mg/cm²)	0.81 mg/cm²（two steps）		1.27 mg/cm²（three steps）	
Targets appearance	Uniform，adherent		Uniform，adherent	



one single step → two steps → three steps

500 ℃ heat treatment for 15min between each deposition

Replace direct current plating by pulse plating ——Pulse Molecular Plating



Typical pulse-current waveform

$$I_p = \frac{I_A}{R}$$

$$f = \frac{1}{\tau_{on} + \tau_{off}}$$

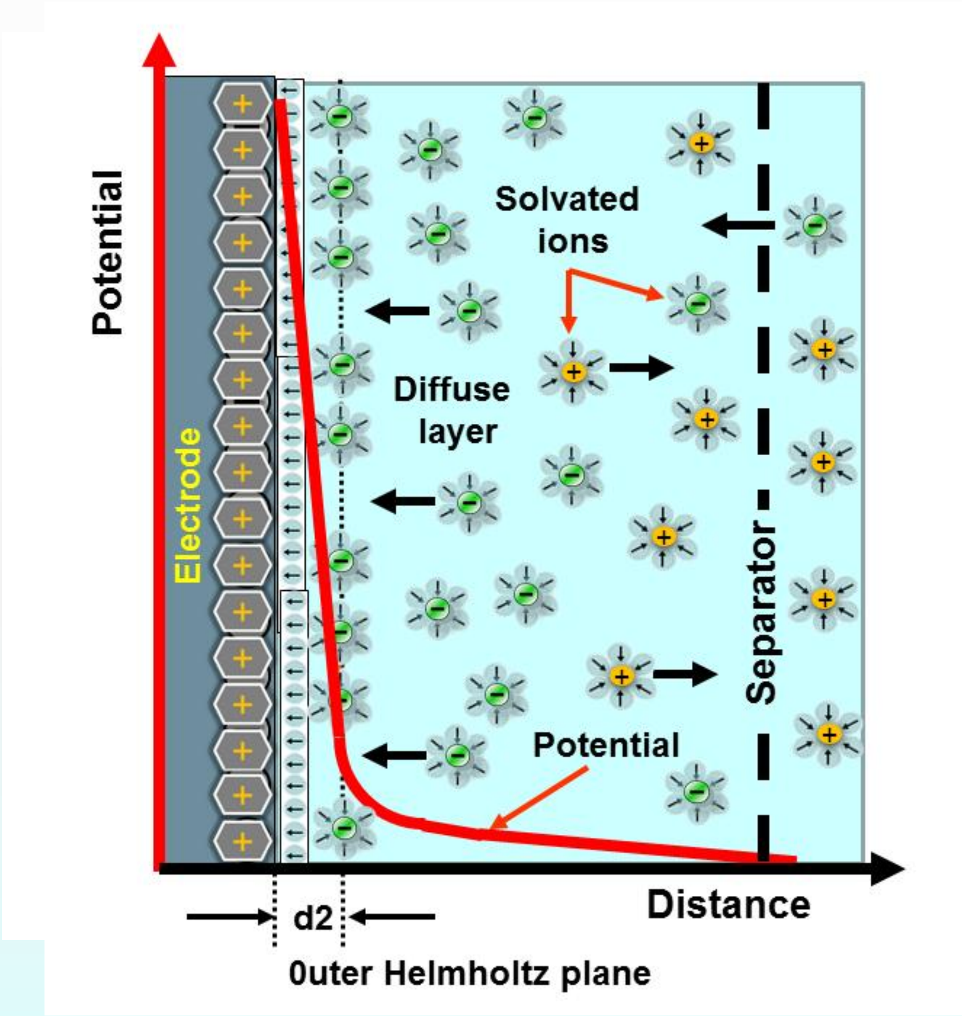
$$R = \frac{\tau_{on}}{\tau_{on} + \tau_{off}} \times 100\%$$

I_A = peak current(I_P) × duty cycle(γ)

I_A : average current
I_P : peak current
R : duty cycle
f : frequency

It has been found that pulse plating has great advangtage for producing the transition metal and noble metal deposit compared to DC plating.
They greatly increase the number of grains per unit area resulting in finer grained deposit with better properties than conventionally Direct Current plating

Advantage of Pulse plating



Simplified illustration of the potential development in the area and in the further course of a Helmholtz double layer.

$$\upsilon = K_1 \exp\left(\frac{-K_2}{|\eta|}\right)$$

η is the crystallization overpotential.

From above equation, it can be inferred that as overpotential increases, the nucleation rate increases resulting in finer crystals.

Find out the deciding factor for pulse molecular plating

frequency —Duty cycle — Average current

$$f = \frac{1}{\tau_{on} + \tau_{off}}$$

$$R = \frac{\tau_{on}}{\tau_{on} + \tau_{off}} \times 100\%$$

$$J_p = \frac{J_m}{R}$$

The difficulty lies in how to scan all the parameters systematically in an efficient way with a minimum of the computational load.

For the purpose, **the orthogonal test method** is introduced to analyze the effect of multi-factors.

Orthogonal array —— L_9 （3^4）

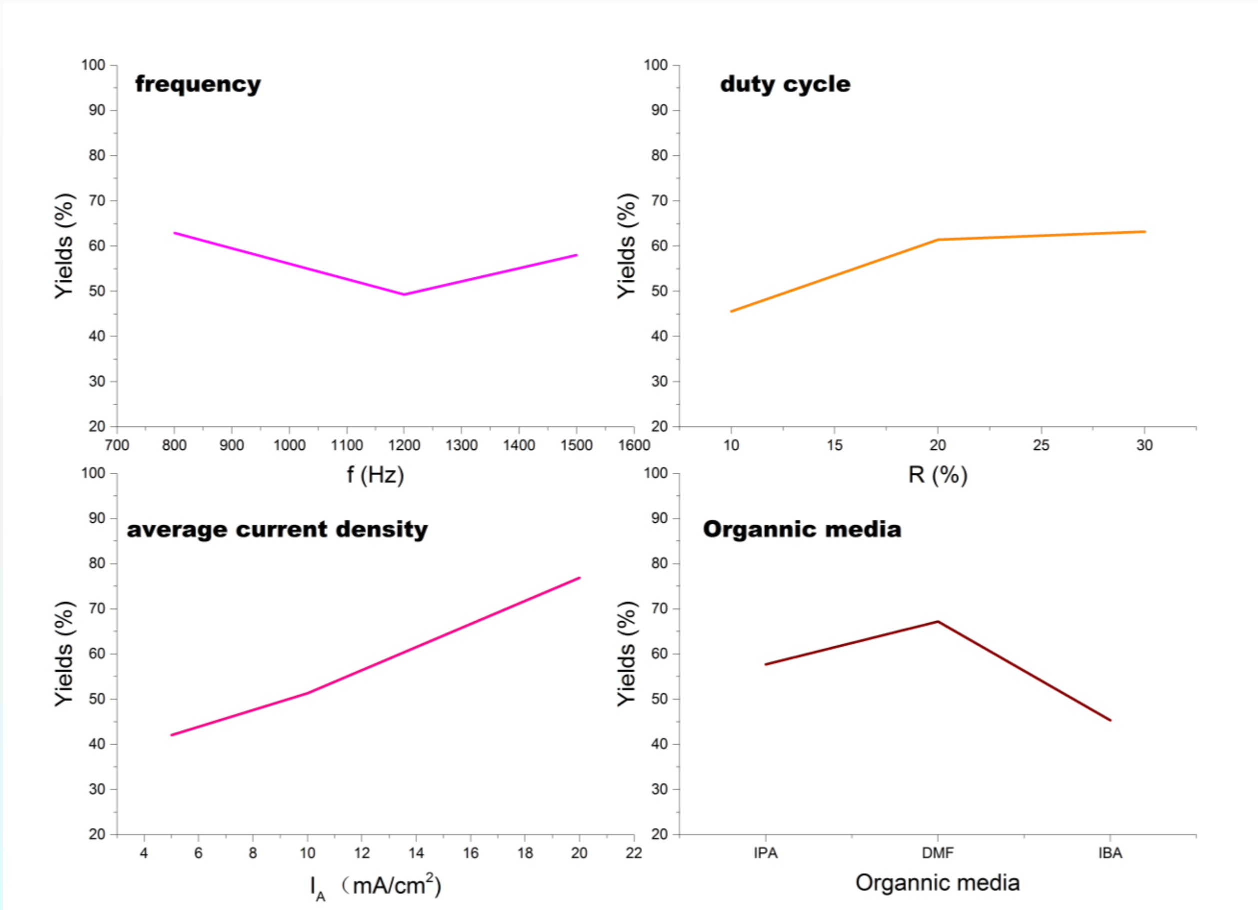
Test case	f（Hz）		R (%)		I_A（mA)		Oganic media		Yield（%）
1	1	800	1	10	1	5	1	isopropanol	37.99
2	1	800	2	20	2	10	2	DMF	72.65
3	1	800	3	30	3	20	3	isobutanol	78.09
4	2	1200	1	10	2	10	3	isopropanol	21.27
5	2	1200	2	20	3	20	1	isobutanol	75.11
6	2	1200	3	30	1	5	2	DMF	51.56
7	3	1500	1	10	3	20	2	DMF	77.43
8	3	1500	2	20	1	5	3	isobutanol	36.60
9	3	1500	3	30	2	10	1	isopropanol	60.04

Orthogonal array —— L_9 （3^4）

Level \ Factor	f(Hz)	R(%)	I_A(mA)	Ogannic media
Ⅰ	188.73	136.69	126.20	173.14
Ⅱ	147.94	184.36	153.96	201.64
Ⅲ	174.07	189.69	230.63	135.96
Ⅰ /3	62.91	45.56	42.05	57.71
Ⅱ /3	49.31	61.45	51.32	67.21
Ⅲ/3	58.02	63.23	76.88	45.32
R	13.60	17.67	34.83	21.89
Optimized level	**800**	**20 or 30**	**20**	**DMF**

Maximum weight factor

The effect of Pulse molecular plating on yields
Deciding factors of Pulse molecular plating



The order of the influences on yield is: I_A > organic media > R > f

The optium conditions can be obtained for the highest yields and deposit quality:

I_A: 20mA

organic media： DMF > IPA > IBA

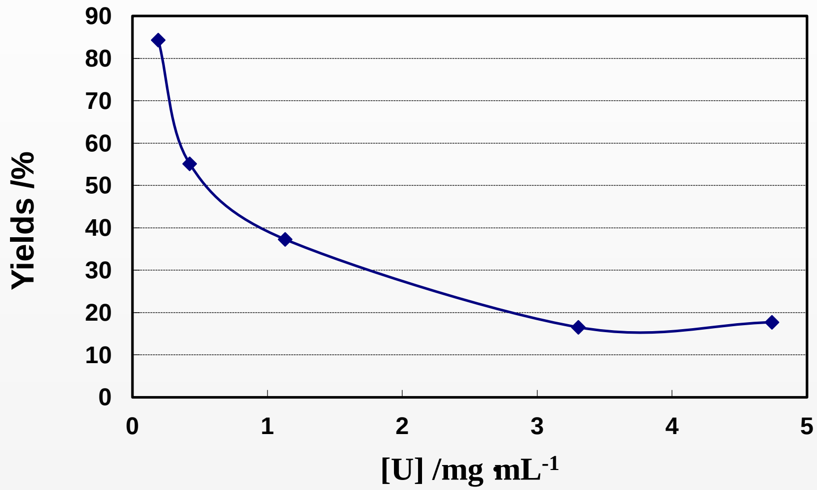
R: 20—30%;

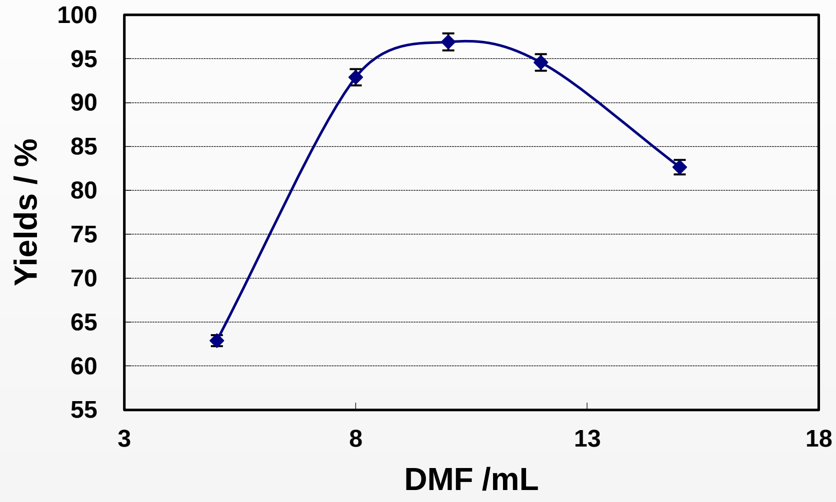
f: 800Hz > 1500Hz >1200Hz

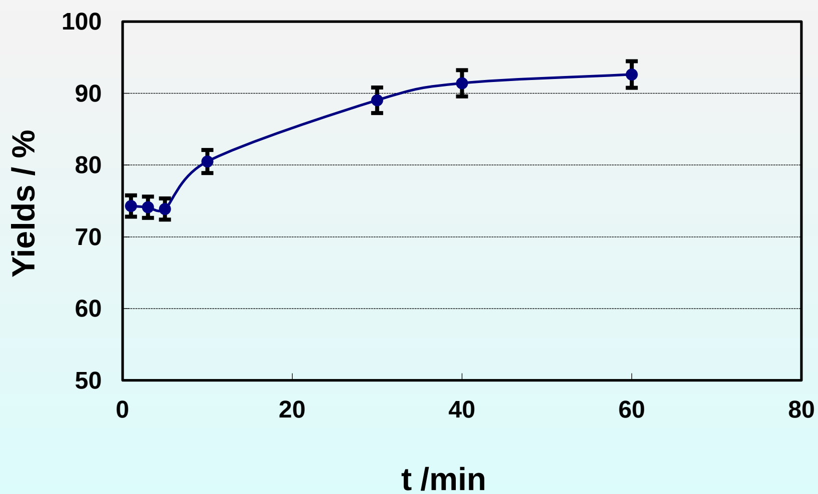
Optimal combinations :

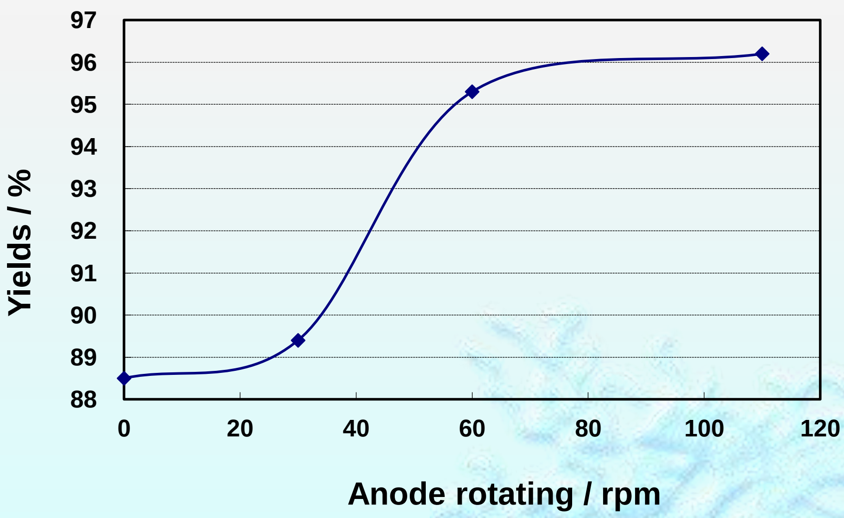
R=20% f = 800Hz I_A = 20mA electrolyte: DMF

Investigation of single plating parameters affecting the yields of uranium



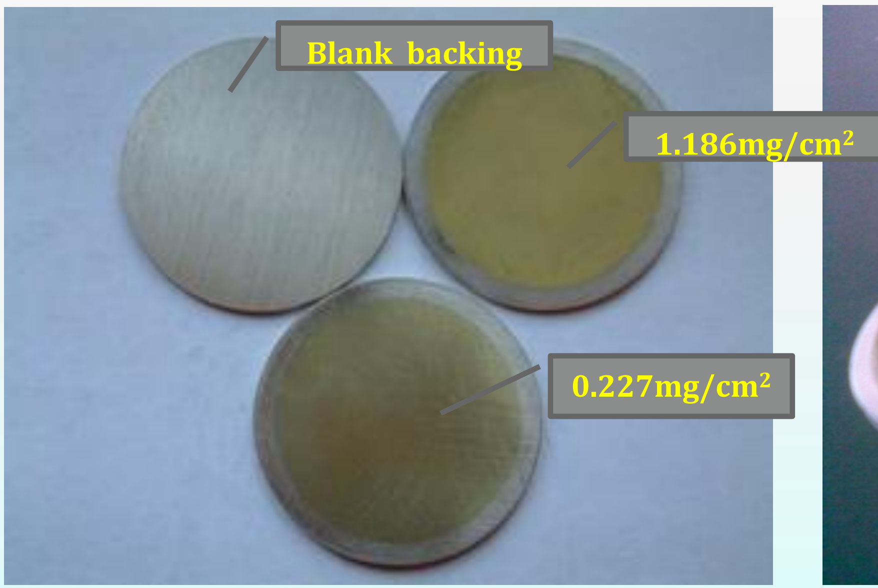


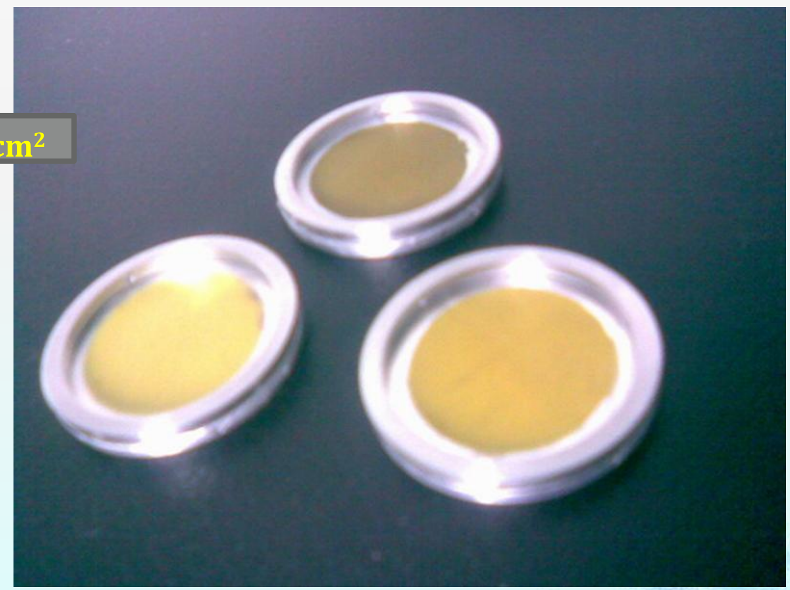




Optimium conditions of Pulse MP for uranium in DMF（N,N-dimethylformamide）

Parameters		Parameters	
Anode	Φ1 spiral Pt	**cathod**	Φ30 stainless steel
Current density	6 mA/cm^2	**Electrode distance**	10mm
f (frequnency)	800Hz	**R (duty cycle)**	20%
Temperature	25℃	**Duration**	30-40min
[U]	0.2-5mg U/mL	**DMF**	10mL





^{238}U,^{236}U targets on stainless steel backing(left) and Al backing(right)

Parameters / Power	f	R	I_A	target thickness
Pulse power-2006	800 Hz	10 %	1-5 mA	1.186 mg/cm^2
Upgraded pulse power-2007	800 Hz	30 %	20 mA	2.500 mg/cm^2

Clearly, there is much room for improvement .

This improved thickness and adherence are attributed to the effect of pulsed current on the process of electrocrystallisation.

In our study, the upper limit of thickness for uranium target is ~2.500 mg/cm^2 .

Targets homogeneity investigations

The homogeneity of uranium targets is determined by two approaches:

- Eddy current thickness meter （Fischer MPOR）
- Low background α-scintillation detector （FJ 414）

1. Target thickness and homogeneity analysis by thickness meter

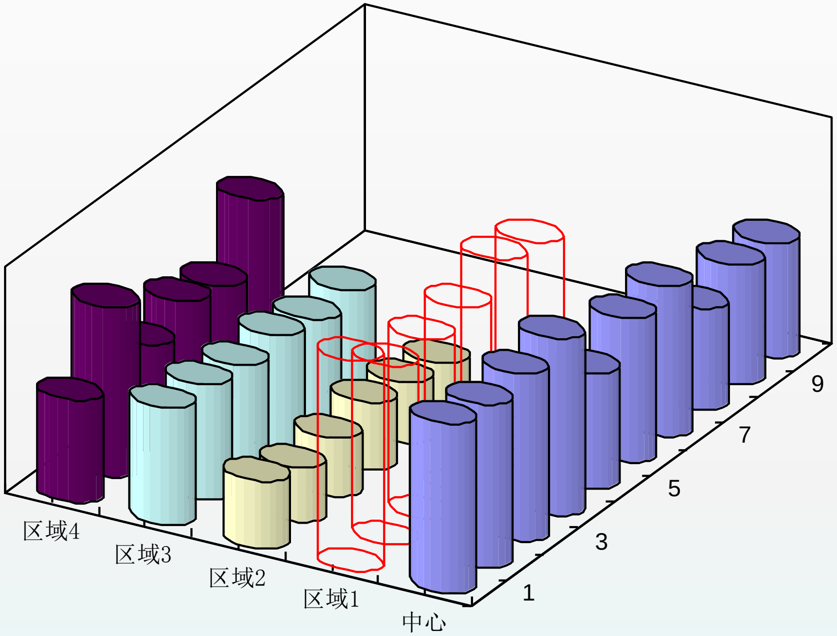
One centre and four regions were randomly selected on a target of 0.227mg/cm^2

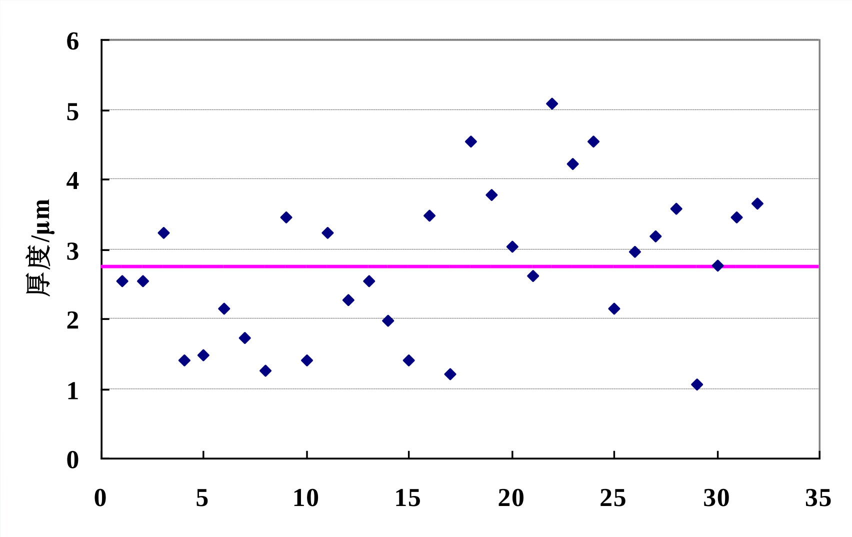
The thickness were measured by an Eddy current thickness meter

Target thickness measurements（0.227mg/cm^2)

Position	Center	Region 1	Region 2	Region 3	Region 4	Average
thickness/μm	3.3	4.2	1.3	2.4	3.4	2.8
S/μm	0.6	0.3	0.1	0.1	0.7	1
RSD%	13	7	10	6	12	39

A target of 0.227 mg/cm^2 was measured

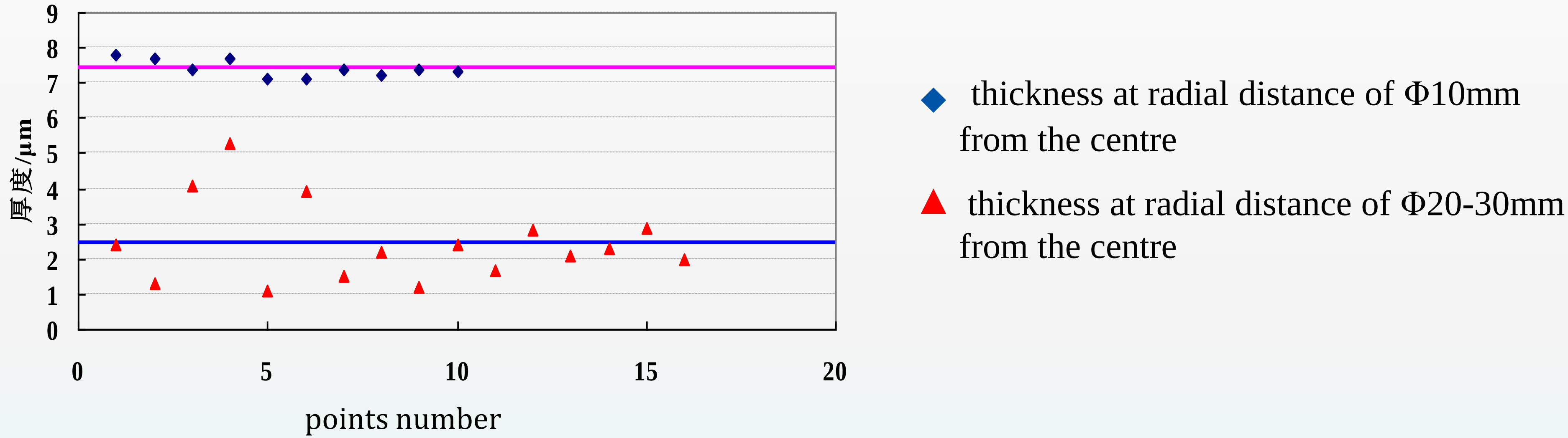




Thickness distribution of U target up to 227μg/cm^2

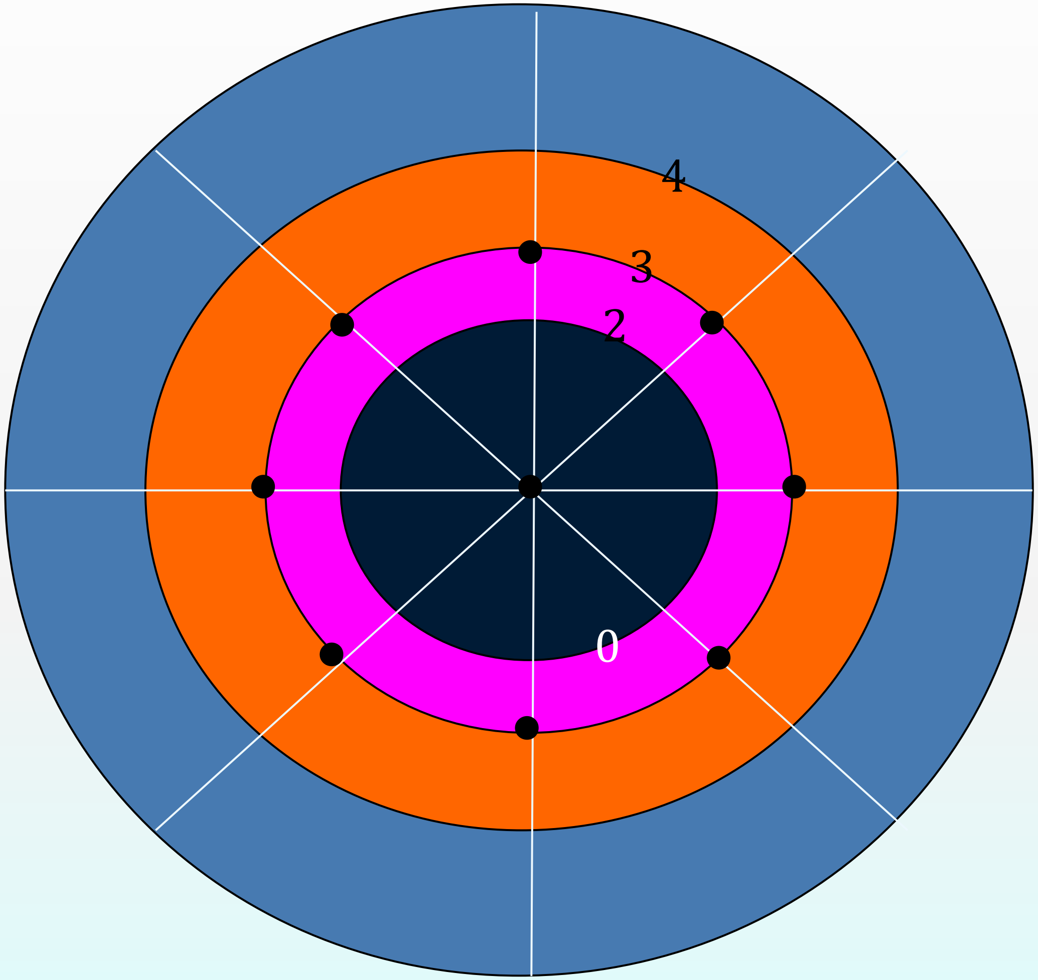
The little deviation in the same selected region indicats that the examined target were homogeneous on a small scale, but not on the whole.

A target of 1.186 mg/cm² was measured



- The average thickness is 7.4μm at radial distance of Φ10mm from the centre
- The average thickness is 2.4μm at radial distance of Φ20~30mm from the centre
- RSD of thinner target thickness is 6~24%, while those for thicker target rose to 6~47%.
- As deposit thickness inceases, the target becomes more inhomogenous. Obviously, Thicker targets (up to 1.186 mg/cm²) are more homogenious in the centre than at the edge.

2. Homogeneity analysis by α-particle counting



A set of masks were prepared for the homogeneity study. The sets consisted of a series of plastic disks with the same size of the target. Each mask disk was dilled a hole of diameter 3mm on the different radial distance. When rotating the disks, the different spots of given radial distance exposed the area of deposit to the α-scintillation detector and the α-particle counting was performed.

Diagram of α-particle counting on the ^{235}U target of diameter 25mm

The black spots(diameter 3mm) are the areas exposed to the α-intillation detector

α-particle counting of ^{235}U targets

Sample No.	counting	RSD%	Sample No.	counting	RSD%
0	7690	5			
2.1-5	8286	4	3.7-3	8951	4
2.2-6	8680	6	3.8-4	8872	4
2.3-7	9028	3	4.1-5	8232	5
2.4-8	8857	4	4.2-6	8267	3
3.1-5	8827	4	4.3-7	8273	4
3.2-6	8630	5	4.4-8	8039	4
3.3-7	8518	3	4.5-1	7952	5
3.4-8	8484	4	4.6-2	8564	4
3.5-1	8459	4	4.7-3	8608	5
3.6-2	9075	4	4.8-4	8126	5

Statistical analysis of α-particle counting

Test item	F test and T test	Results
20 spots （except center）	$F=2.31>F0.05(19,40)=2.00$	inhomogeneous
Third round	$F=2.41<F0.05(7,16)=2.66$	homogeneous
Fourth round	$F=2.62<F0.05(7,16)=2.66$	homogeneous
Compared the third circle with the fourth circle	$T=4.02>t0.05(14)=2.15$	significant differance

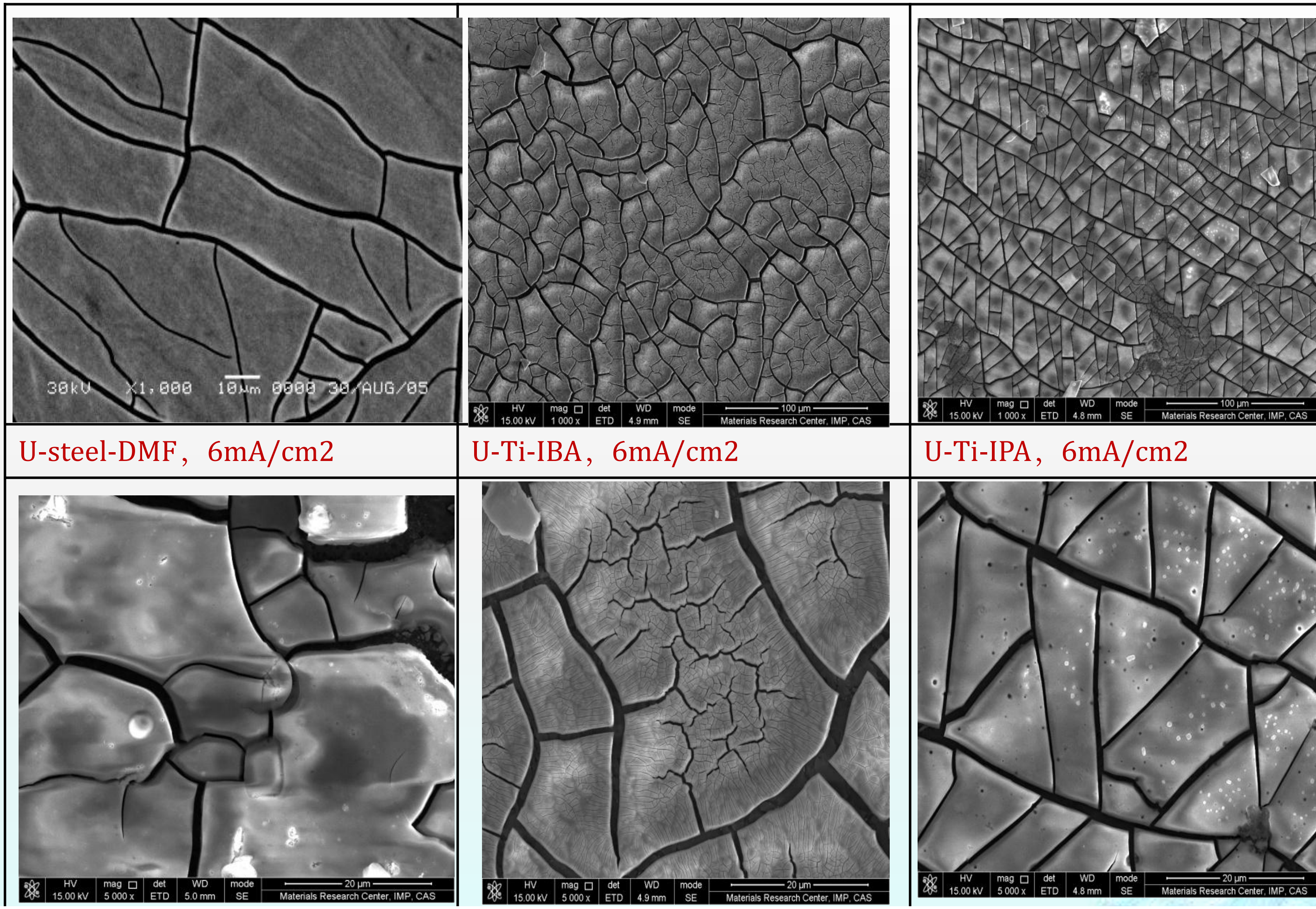
The results of statistical analysis shows that on the identical radial distance, the counting value of measured spots are roughly coincident， indicating a homogeneous thickness distribution, but those on the different radial distance shows significant differance.

The target thickness is inhomogeneous over the whole area.

while relatively high homogeneity occurs on the identical radial distance.

The radial distribution pattern implies that inhomogeneity may be attributed to the round shape electric field resulting from the spiral Pt anode.

Surface morphological investigartion of U deposits



×1000 times magnified (top row); ×5000 times magnified (bottom row)

U-steel-DMF，6mA/cm2　　U-Ti-IBA，6mA/cm2　　U-Ti-IPA，6mA/cm2

The mud-cracking of the surfaces seems to be related to the volatility of the used solvent.
Less volatile DMF solvent yields smooth and less crack Nd targets.
boiling point: 153℃>107.6℃>82.2℃ (DMF>IBA>IPA)

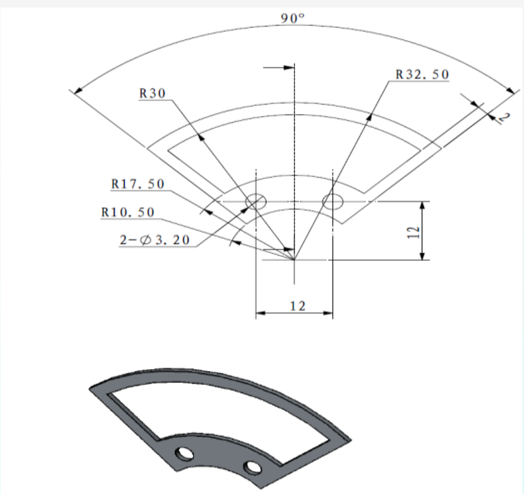
conclusion

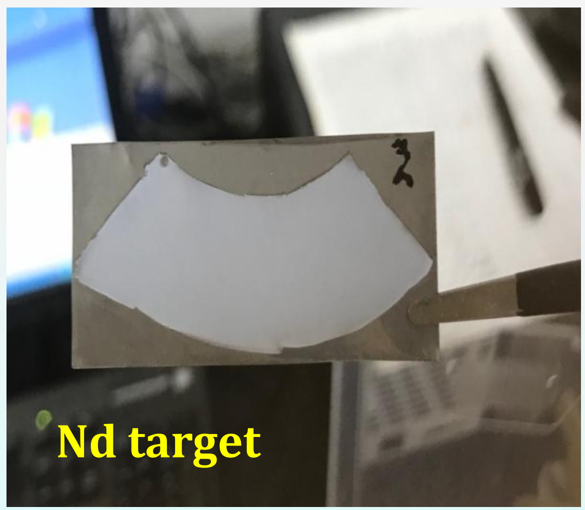
- Electrode shape has a significant impact on layer thickness homogeneity.
- Deposit quality and yield are all strongly influenced by current density. The applied plating solvent has effect on the surface morphology
- The thickness of targets up to 200 μg/cm^2 irregularly distributed over the whole area
- The layer thickness homogeneity was not be improved by pulse molecular plating technique.
- Above 2.500 mg/cm^2 , increasing electrical resistance of layer hinders further deposition and the deopsit turned into loose powder after drying.
- Both thin and thick target exihbit similar trend on radial thickness distribution.

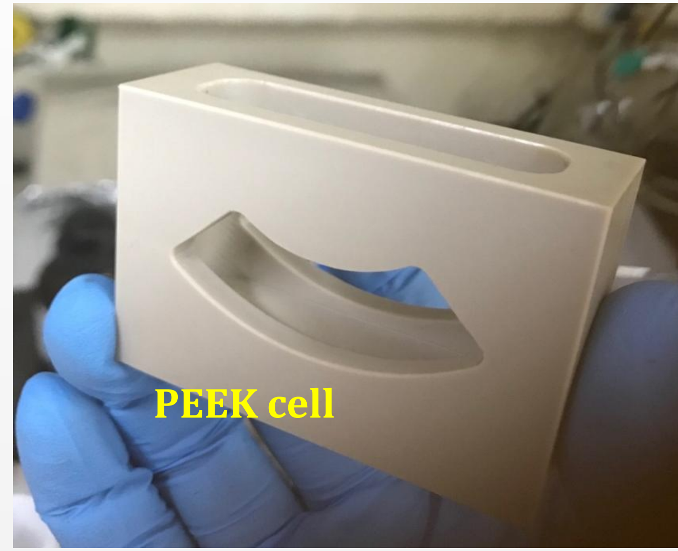
- **What pulse palting technique contributes to the molecular plating seem to be the improved deposition yields or thickness and adherence of the target compared to direct current (DC) plating .**
- **Current density distribution depends only upon the cell geometry, which significantly affects the layer homogeneity.**

Targets preparation for rotating wheel system with a multi-target device

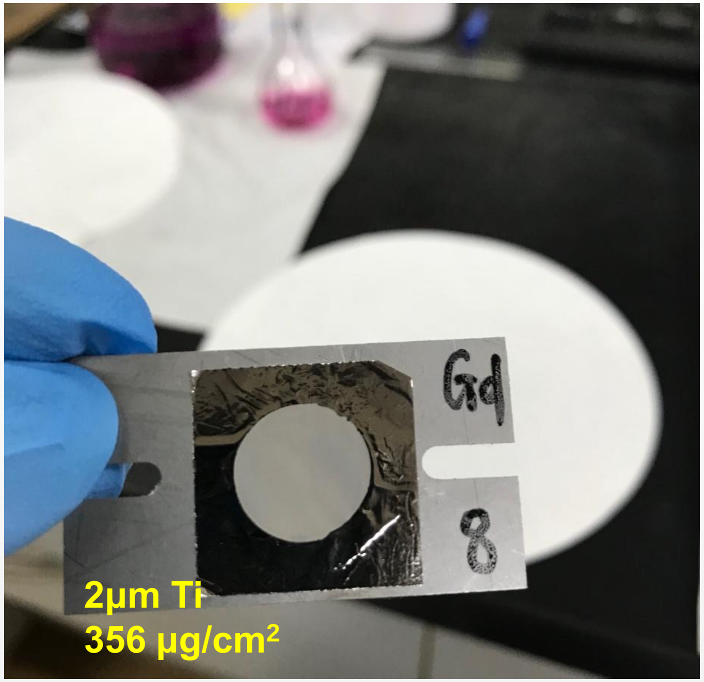
- m(^{243}Am)=10 mg, S_{target}=4.66 cm^2,
- 1.708mg ^{243}Am/per target
- 400ug/cm^2 of Nd targets was prepared as a
- model electrolyte for ^{243}Am

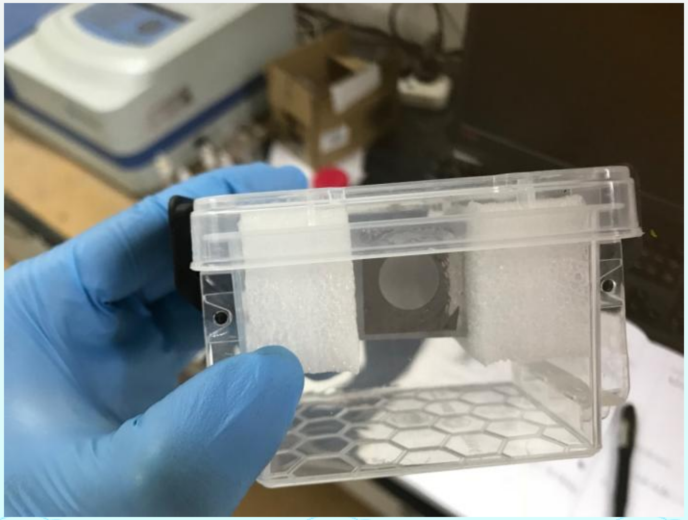






Gd targets for reaction of $^{160}Gd(^{40}Ar,4n)^{196}Pb$

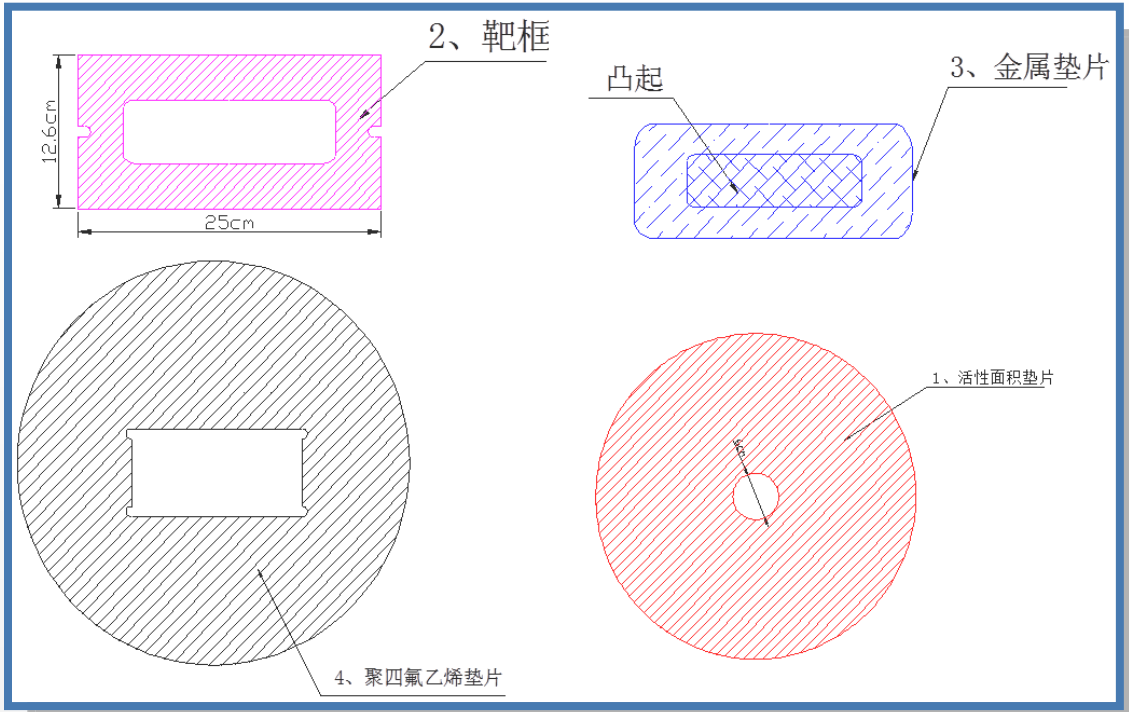




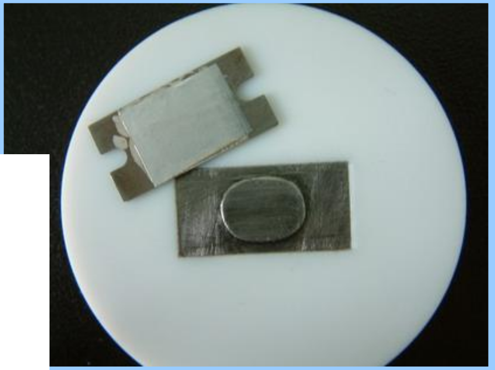
Optimum condition for Gd by MP method

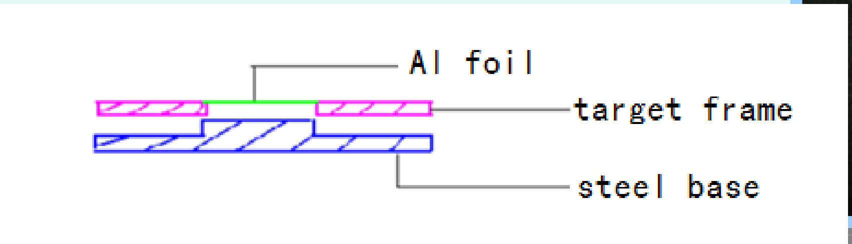
Diameter	12.3 mm
Area	1.226 cm^2
Anode	10-μm thick Pd foil
Cathode	2-μm thick Ti foil
Current density	4 mA/cm^2
Constant current	5 mA
Initial voltage	500 V
Temperature	17℃
Deposition time	15 min
Yield	76%

Electrolyte solution:
13mL isopropanol
65uL Gd-2 stock solution (9.42 mg Gd/mL, 0.2M HNO3)
$Volume_{H2O}$% =0.5

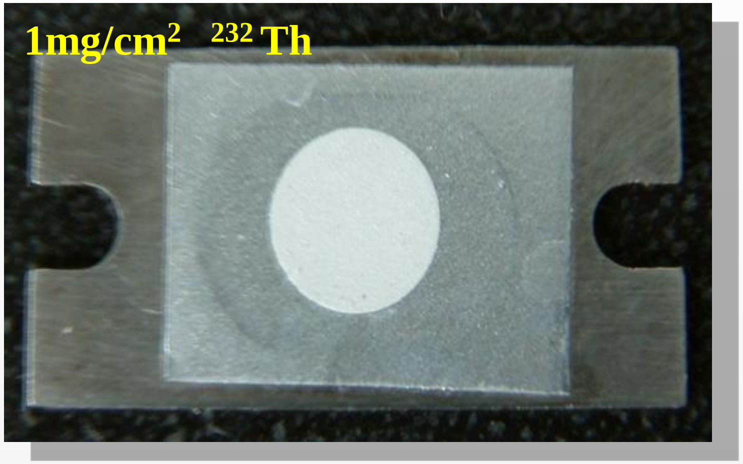


1、Teflon mask (depostion area is defined)
2、Target frame
3、Steel base
4、Teflon support

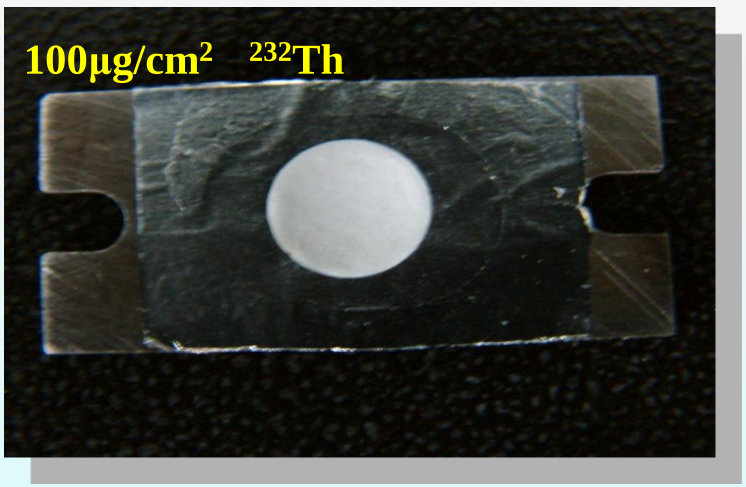




^{232}Th targets for measurement of ^{232}Th(α,2n)^{234}U cross section



1mg/cm^2 on 10 μm Al



100μg/cm^2 on 2 μm Al

Optimum condition for Th by MP method

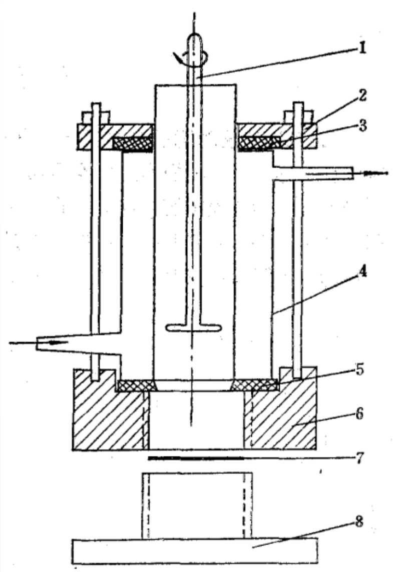
Diameter	6mm
Area	0.28 cm^2
Anode	Φ1 spiral Pt wire
Cathode	2 or 8-μm thick Al foil
Current density	3.5-7.0 mA/cm^2
Constant current	2 mA
Initial voltage	600 V
Temperature	17℃
Rotation rate	60 rpm
Deposition time	15 min
Yield	97%

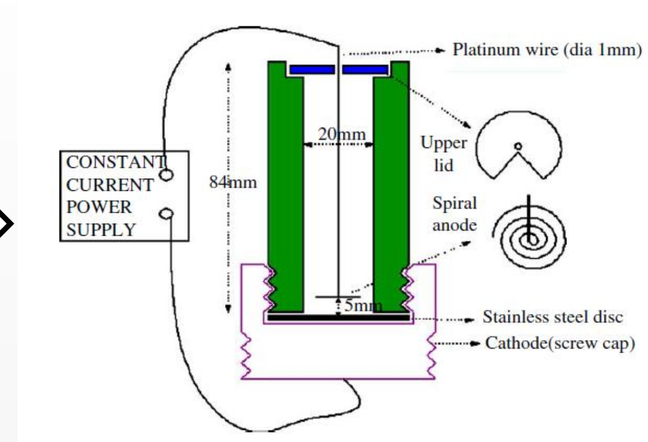
Procedure:

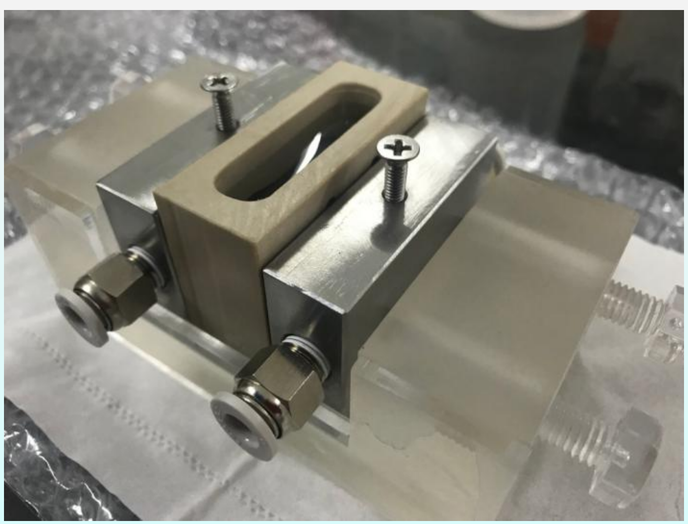
An aliquot of Th stock solution was heated to dryness with the infrared lamp, then disolved

An aliquots of the Th stock were evaporated to dryness by a heating plate . The residue was dissolved in 80uL 0.04M HNO3 and 8mL isopropanol was added.

Volume$_{H2O}$% =1.0







The evolution of plating cells we used in the target preparation

Summary

- Pulse plating technique was applied in the molecular plating for the first time. It suggested a promising approch to further improve the quality and thickness of actinids targets. Atinide targets can be prepared without repeated deposition procedure.
- Target thickness analysis and surface morphological investigartion were performed to elucidate the influence on the target homogeneity.
- More detailed investigations for Pulse Molecular Plating are still required, such as the grain size at different pulse period(Influence of charge and discharge of electric double layer(EDL) and influence of the peak current density on the morphology.

Thanks for your attention!