

Электрохимическое получение функциональных материалов



Контролируемость

Возможности мониторинга по электрохимическим откликам

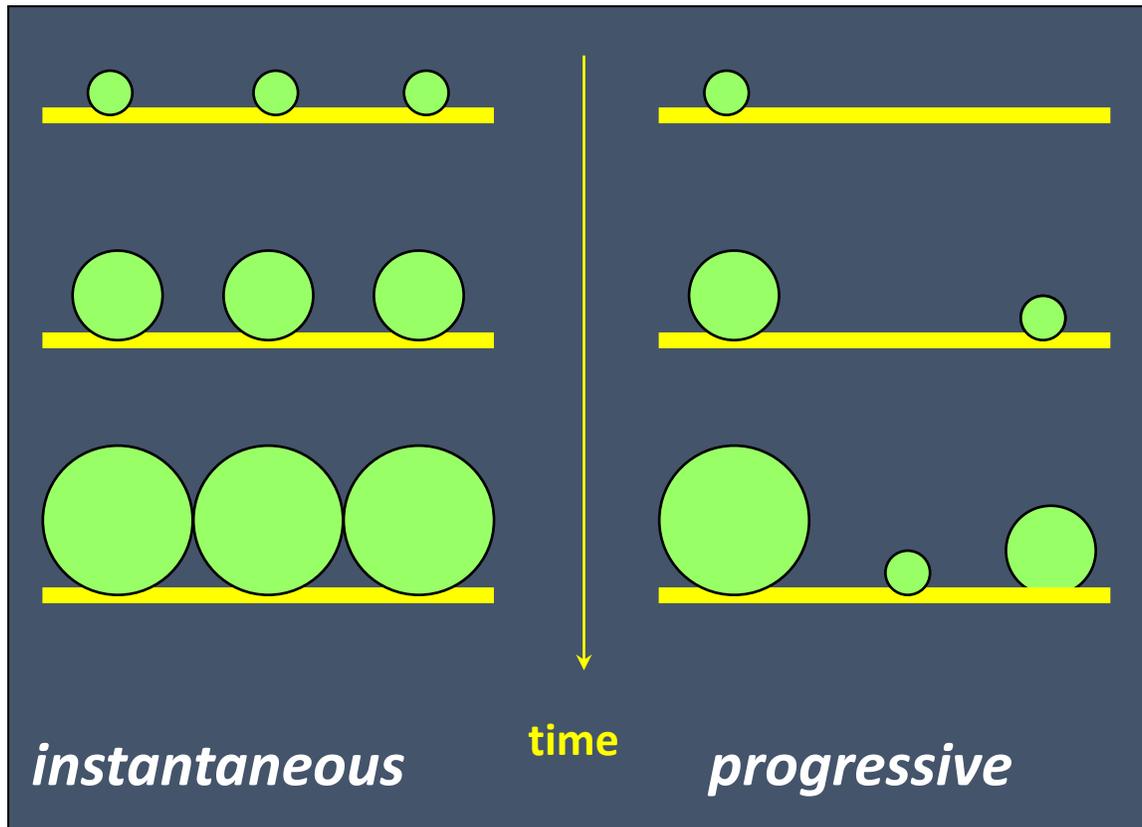
Гибридные технологии

Активные центры нуклеации (зарождения) при электрокристаллизации

$$N = N_0 [1 - \exp(-At)] \longrightarrow I = nFkS(t).$$

Перекрывание

$$I = \text{const} \cdot t^n \exp(-\text{const}' \cdot t^m)$$



МГНОВЕННАЯ

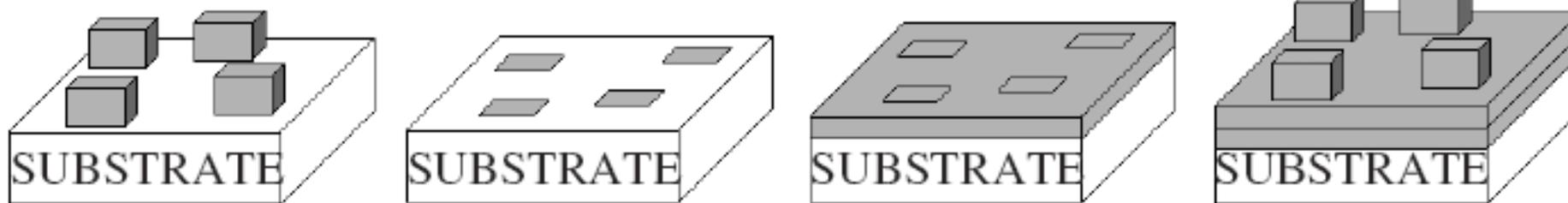
instantaneous

time

progressive

прогрессирующая

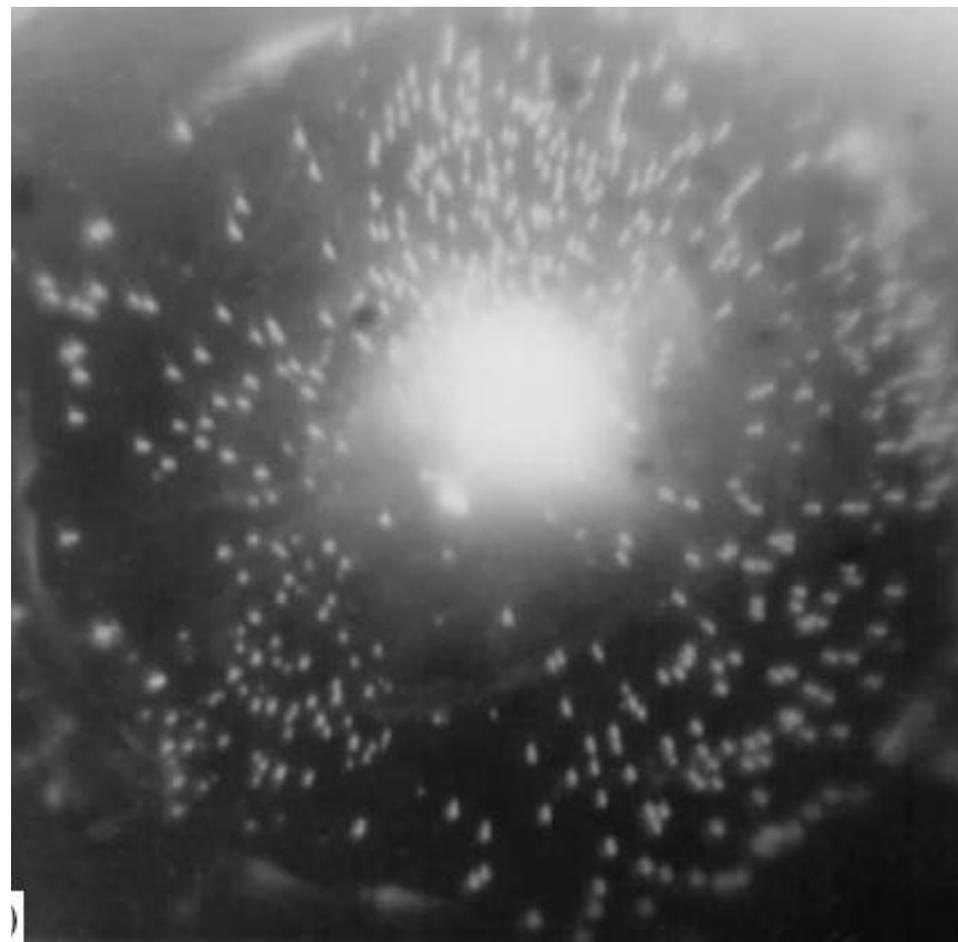
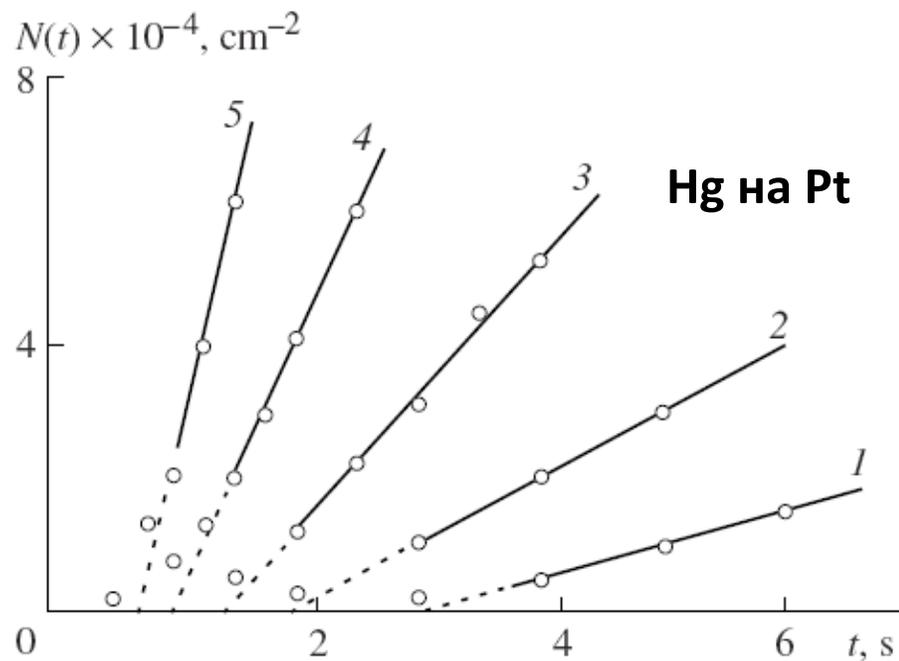
$M(t)$ – по закону
Фарадея



Нуклеация – на инородной подложке или на слое адатомов



Пример «прогрессирующей»
нуклеации:



Зависимость от потенциала E

Замедлена стадия
переноса электрона

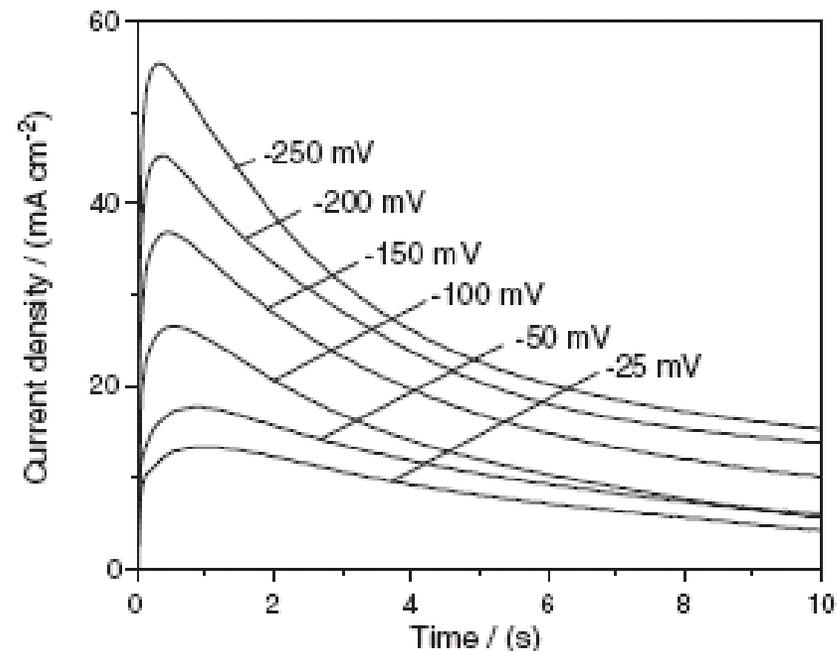
$$E = a + b \log i$$

Замедлена стадия
подвода реагента

$$i = i_{dif}(c_{local})$$

Скорость процесса
(плотность тока)

$$i = I/S$$

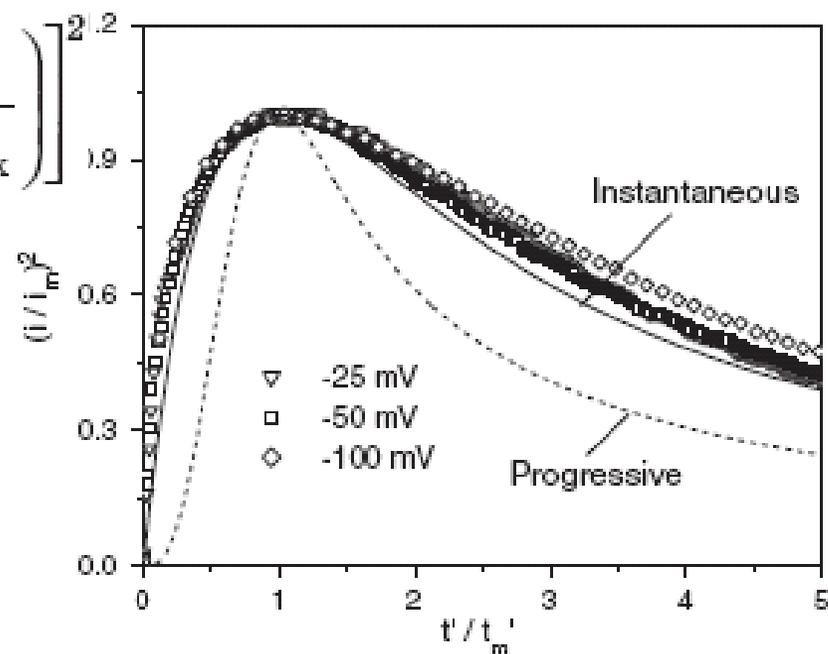


Модель
Шарифкера

$$\left(\frac{I}{I_{max}}\right)^2 = 1,9542 \frac{t_{max}}{t} \cdot \left[1 - \exp\left(-1,2564 \frac{t}{t_{max}}\right)\right]^{2,2}$$

Вид приведенного транзientа
зависит от

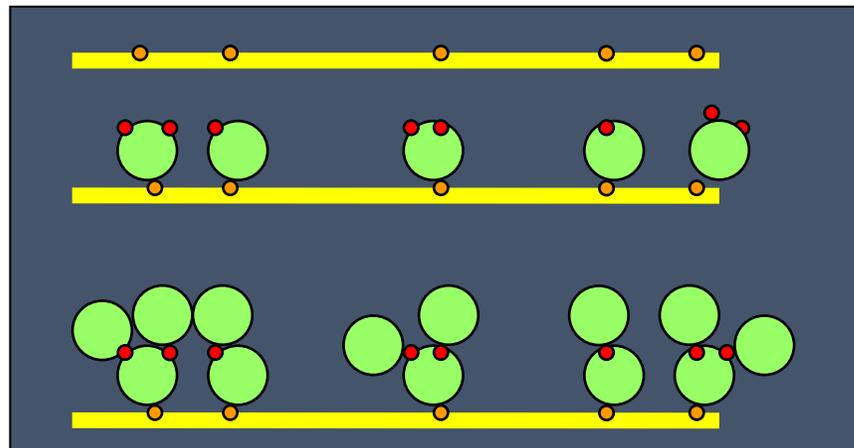
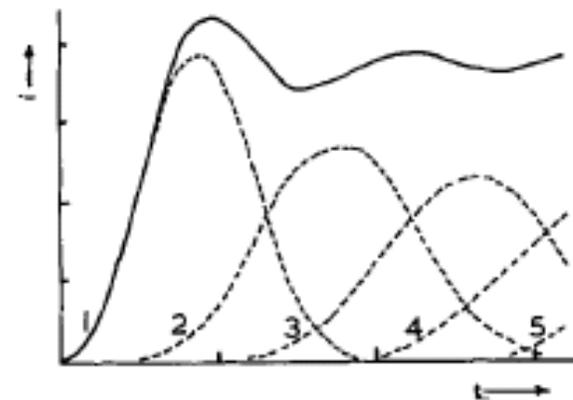
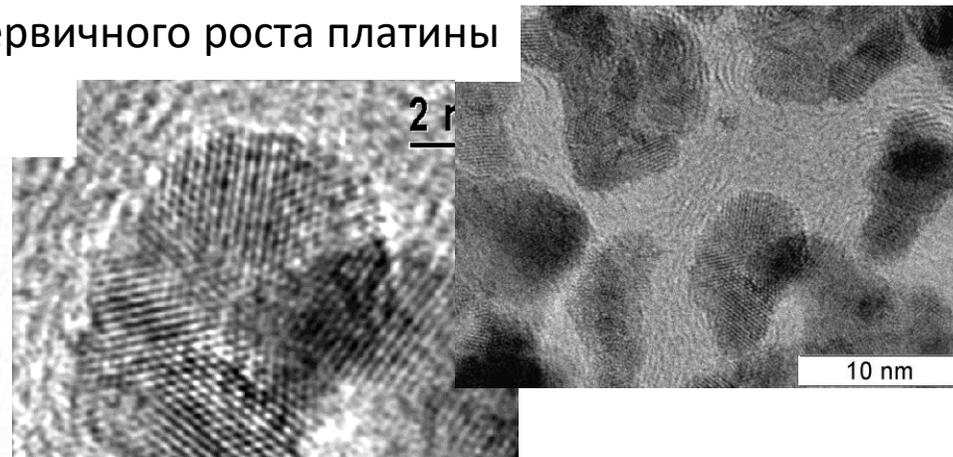
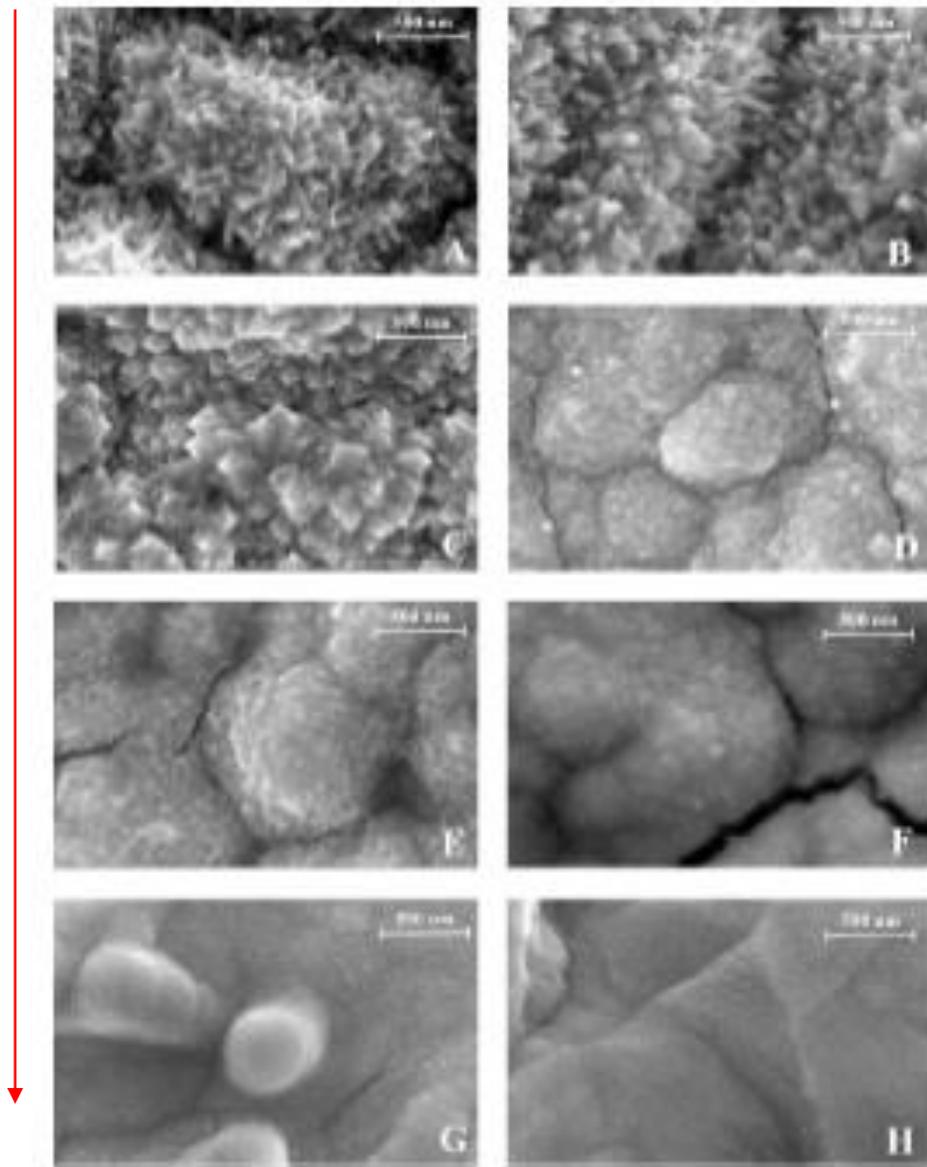
- природы медленной стадии
- геометрии зародыша
- геометрии роста



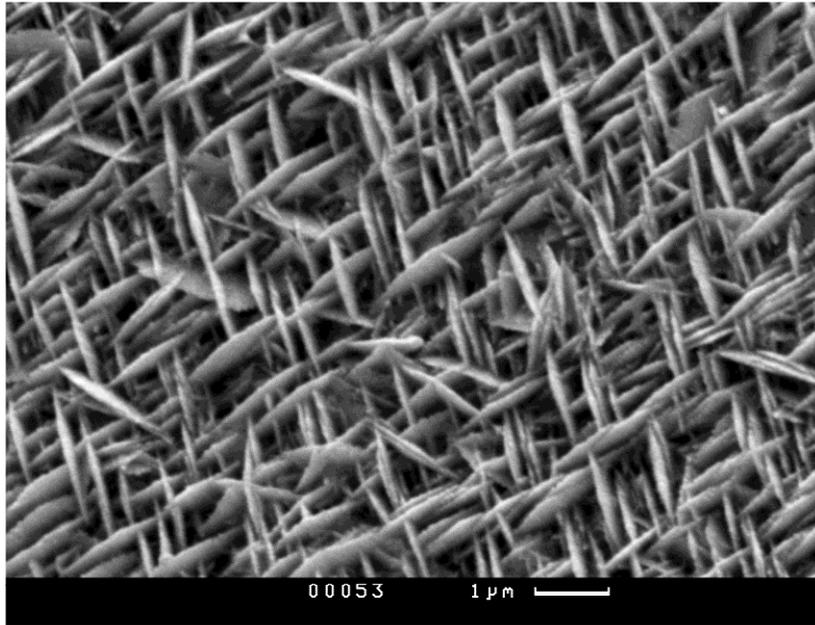
Электродиспергирование

Вторичная нуклеация при ингибировании
первичного роста платины

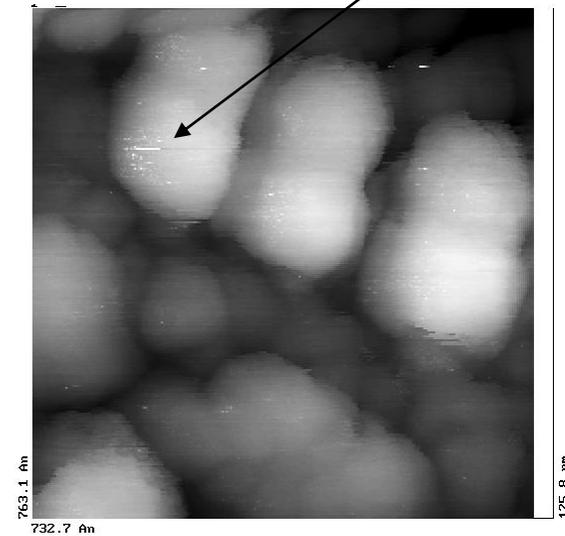
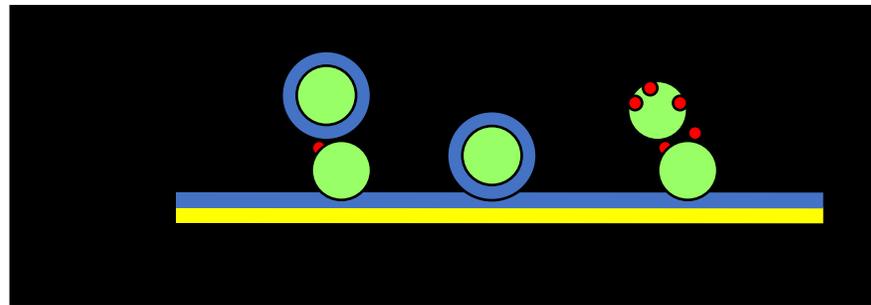
E



Квазиплатирование: палладий - полиэтиленгликоль



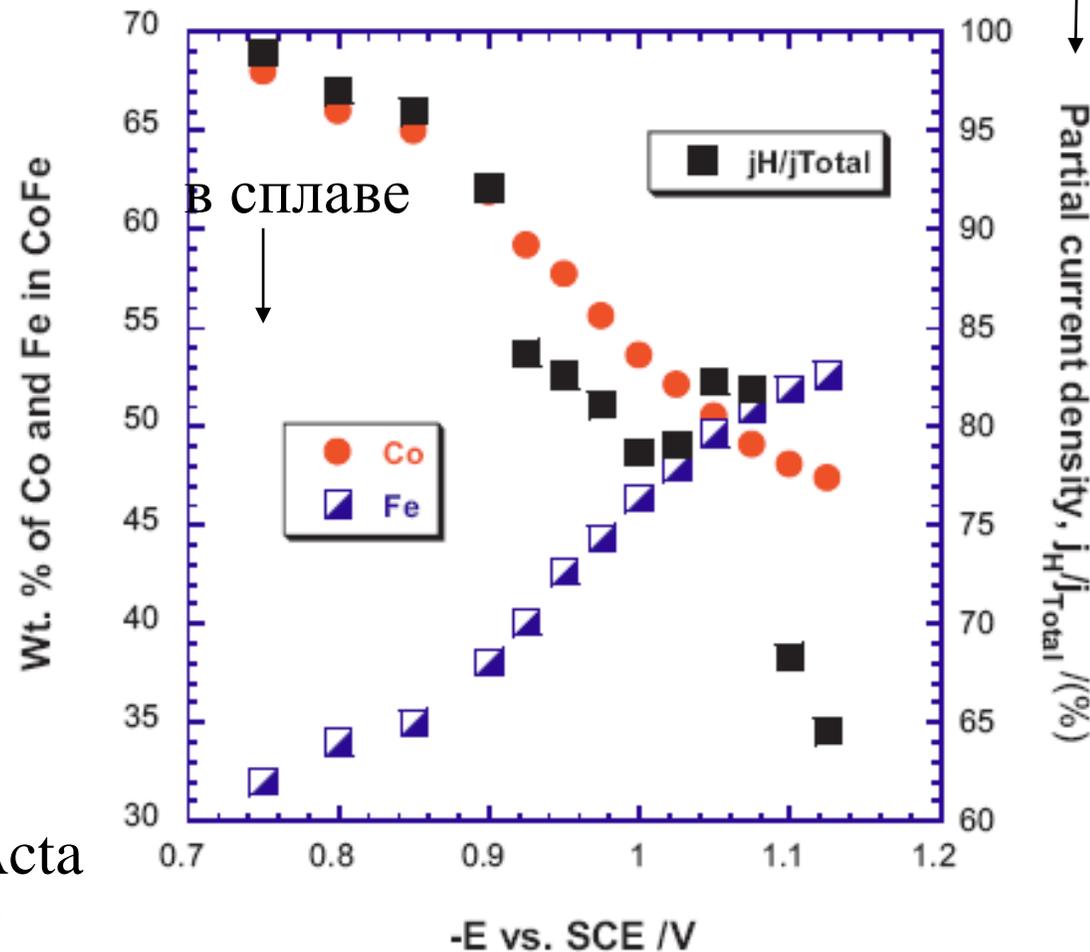
5 nm



Composition of the plating solution.

Compound/condition	Value
NH ₄ Cl	0.3 M
H ₃ BO ₃	0.4 M
Saccharin as Na-salt	0.004 M
CoSO ₄ ·7H ₂ O	0.05 M
FeSO ₄ ·7H ₂ O	0.0072–0.065 M
pH	2.3 ± 0.02
Temperature	23 ± 0.5 °C

Осаждение сплавов
(параллельный процесс:
выделение водорода)

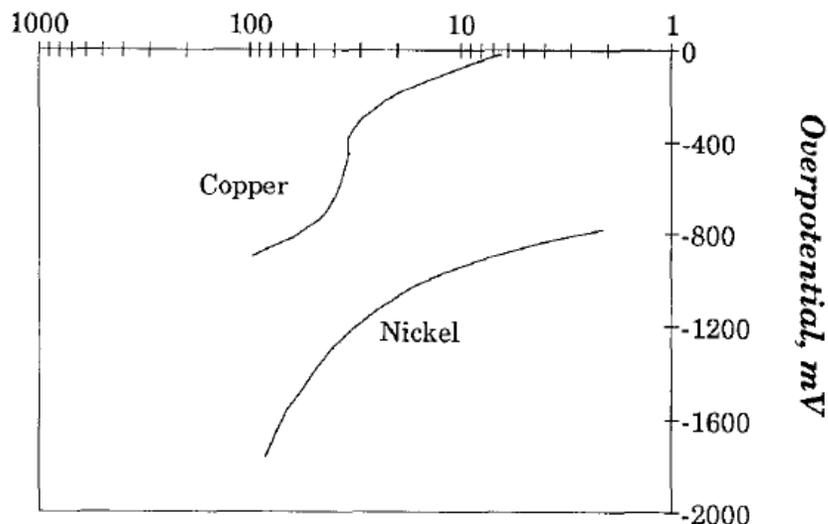


Electrochimica Acta
58 (2011) 25–32

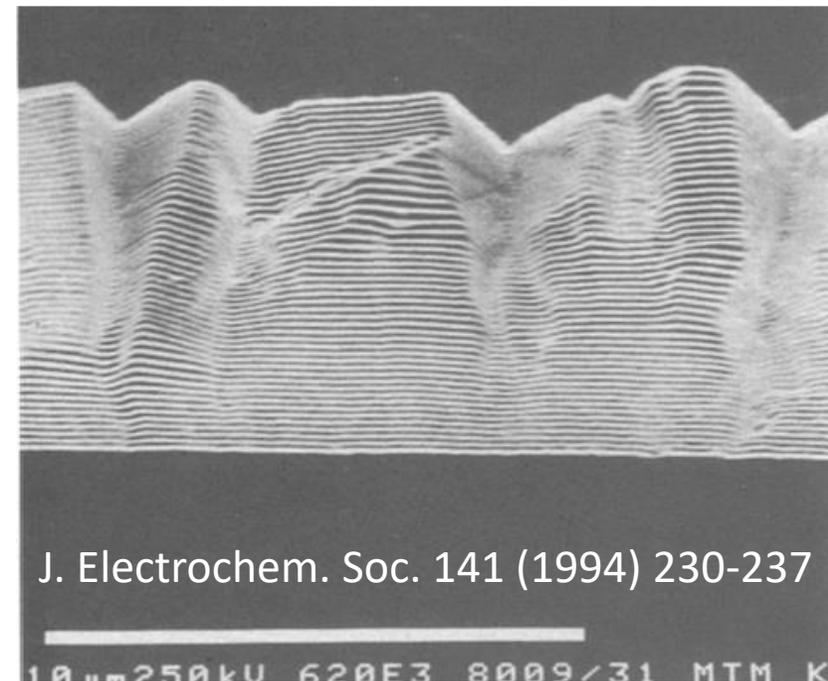
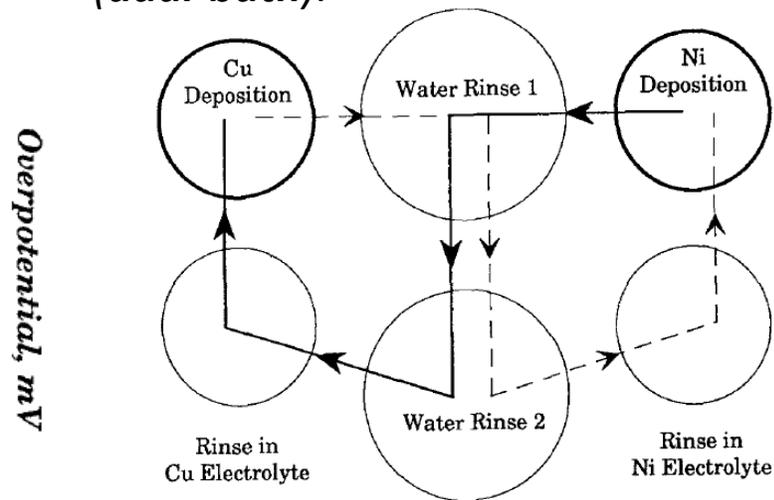
пример

Осаждение биметаллических сверхрешеток

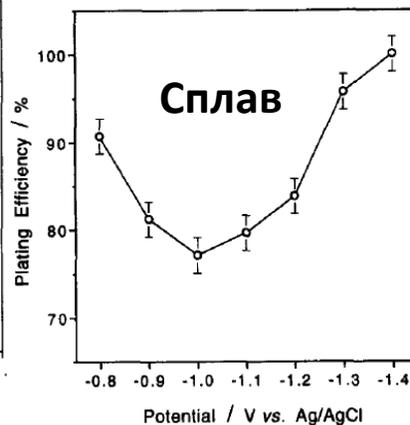
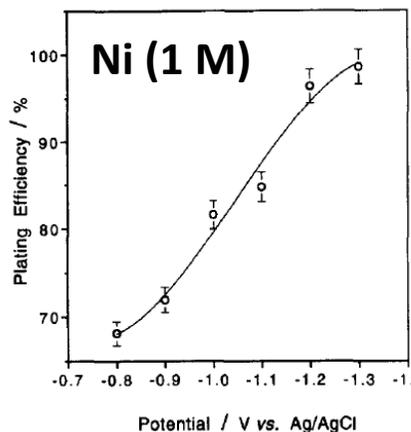
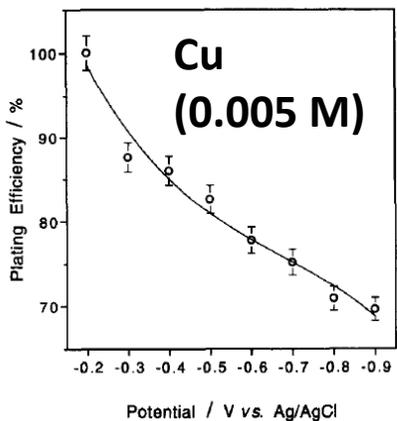
Cathodic Current Density, mA/cm²



Поочередно, с отмывкой (dual-bath):



Single-bath: более низкая концентрация «благородного» компонента, двух- и многоступенчатые режимы



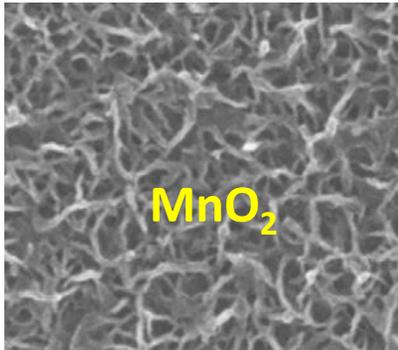
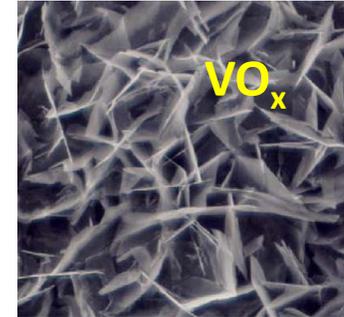
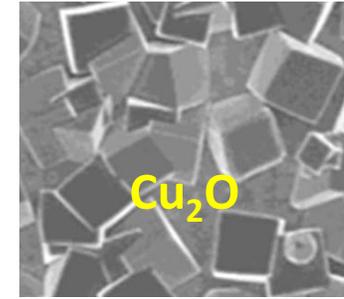
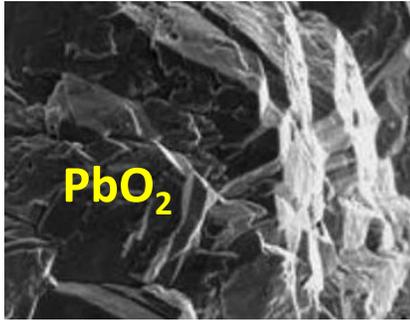
Atomic concentrations in Cu–Ni alloy thin films as a function of deposition potential ^a

Deposition potential / mV vs. Ag AgCl	Copper %	Nickel %
-700	100.00	0.00
-800	70.40	29.60
-1000	28.15	71.85
-1100	16.94	83.06
-1200	13.91	86.09
-1300	8.35	91.65

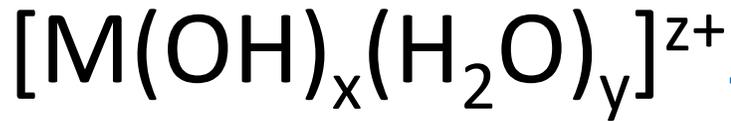
J. Electroanal. Chem. 398 (1995) 5-12

Осаждение оксидов, необходимые условия:

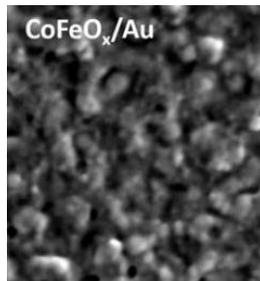
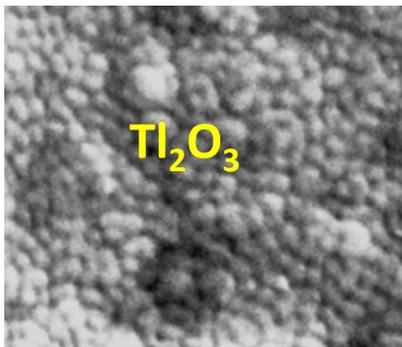
- минимум две степени ненулевых степени окисления;
- среда, в которой соответствующие соединения имеют существенно разную растворимость;
- проводимость осаждаемого оксида.



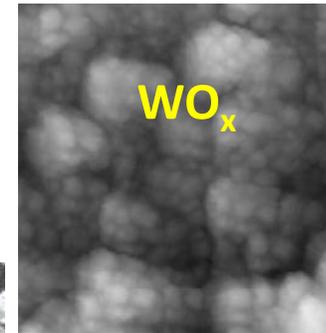
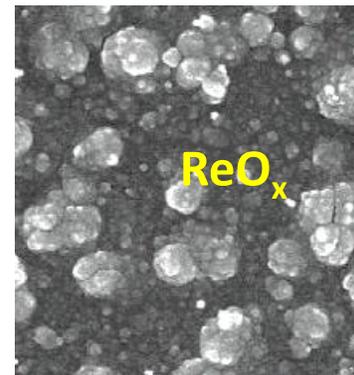
**Анодная
электрокристаллизация**



**Катодная
электрокристаллизация**



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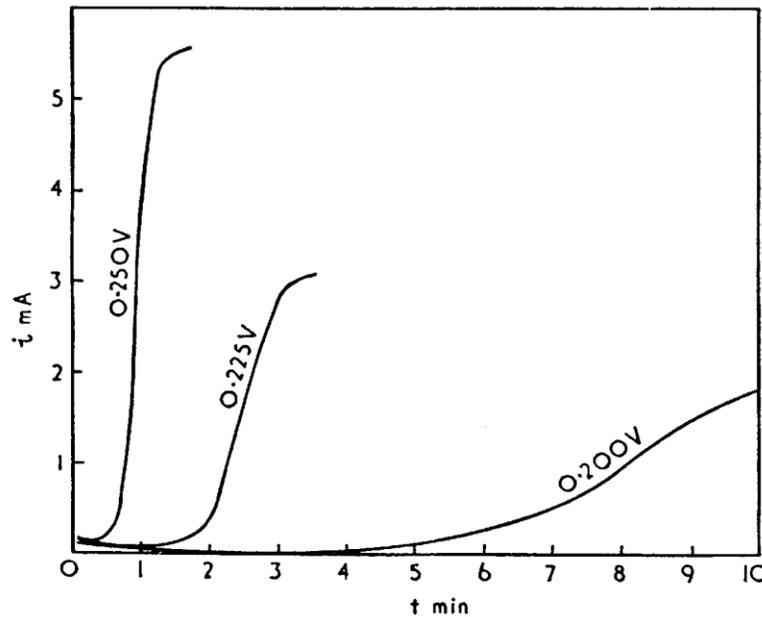
THE ANODIC OXIDATION OF SOLUTIONS OF PLUMBOUS SALTS

Анодная электрокристаллизация
(диоксид свинца)

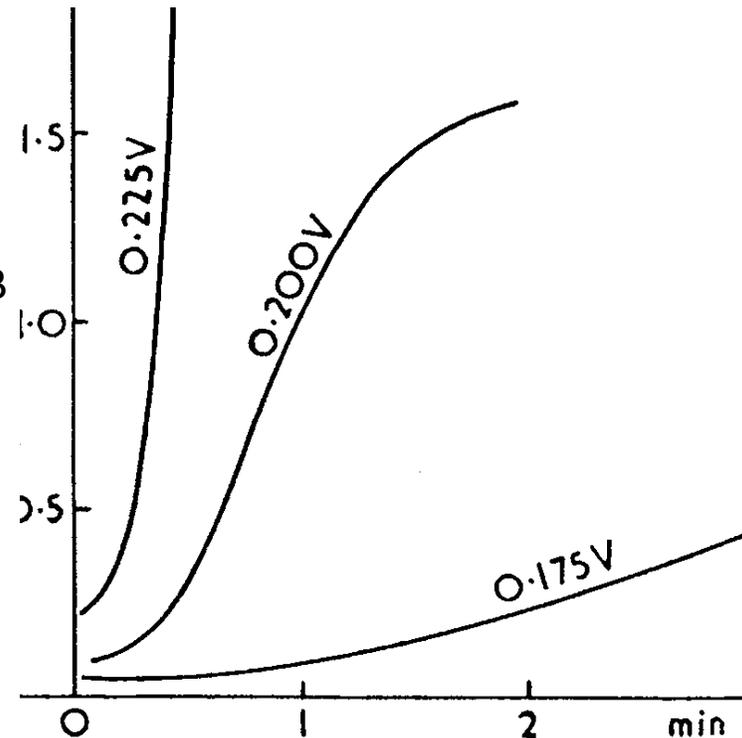
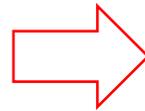
PART 1.—THE KINETICS OF DEPOSITION OF α -LEAD DIOXIDE FROM ACETATE SOLUTIONS

Trans. Faraday Soc.
54 (1958) 1370-1381

BY M. FLEISCHMANN AND (MISS) M. LILER

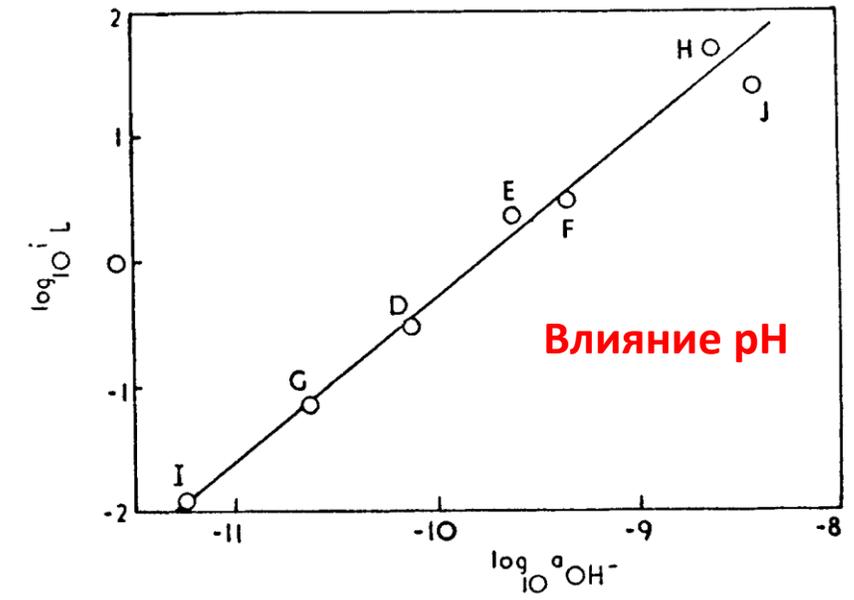
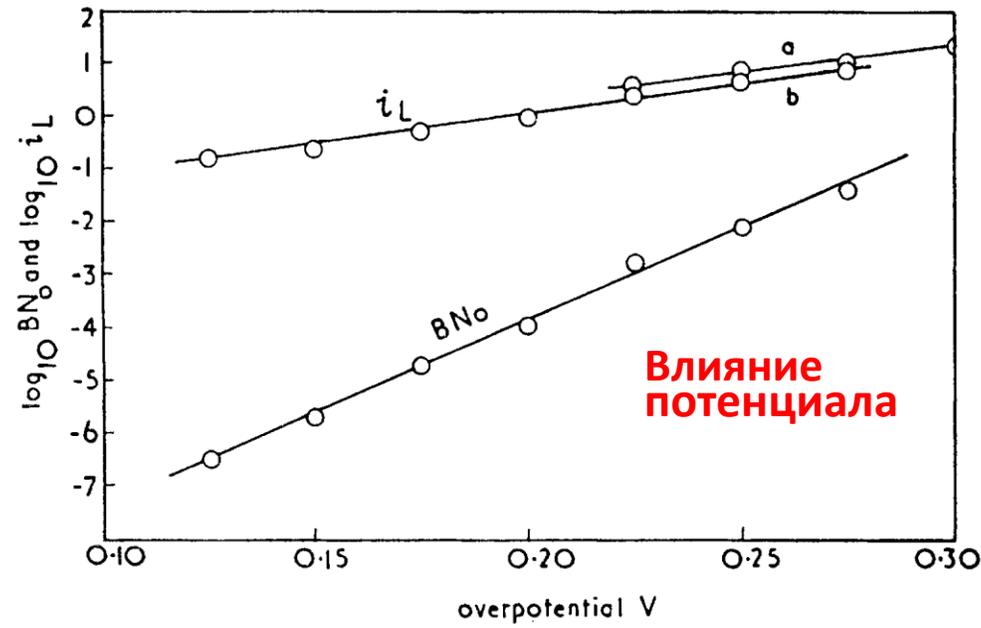
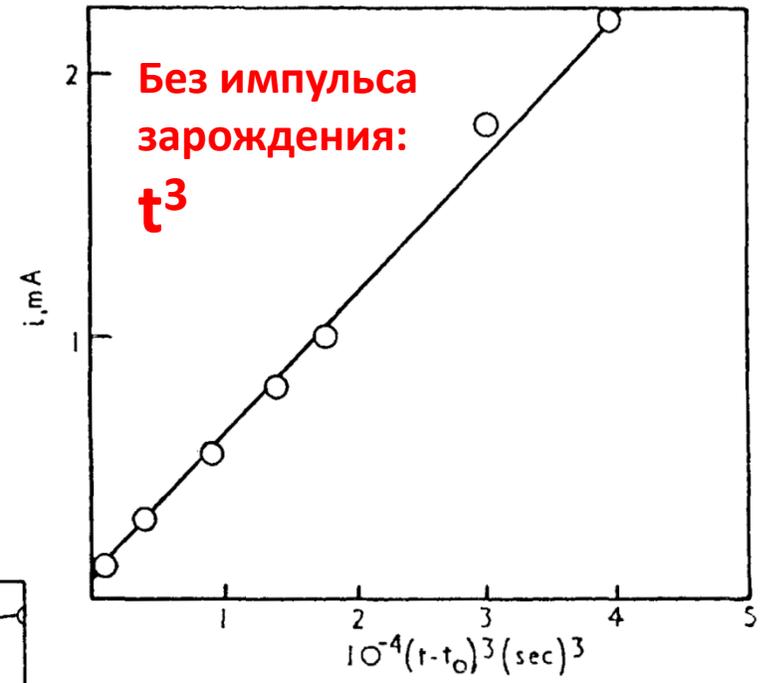
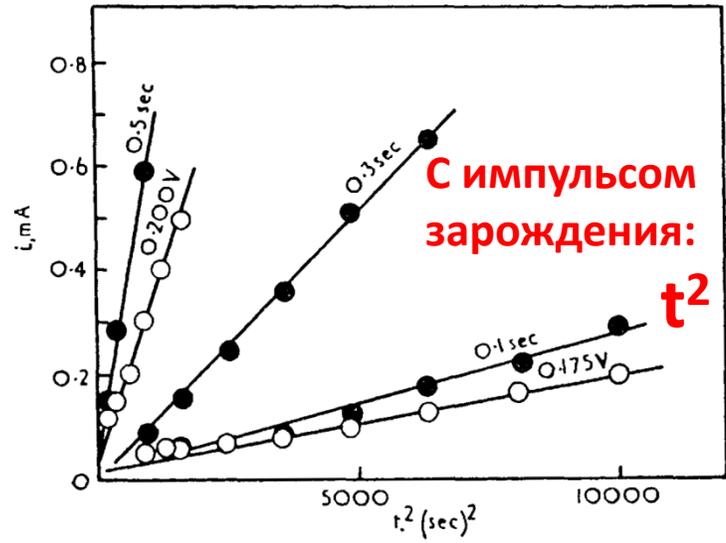


0.1 с
при 0.4 В

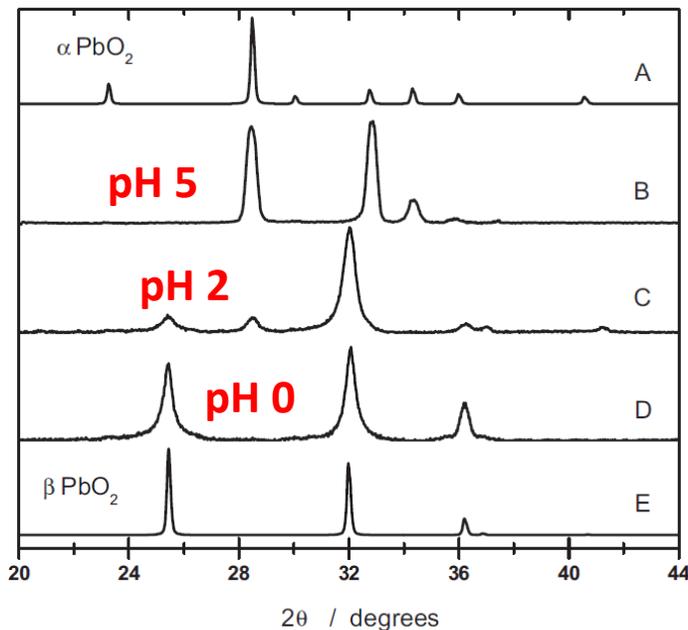


$$N = A't,$$

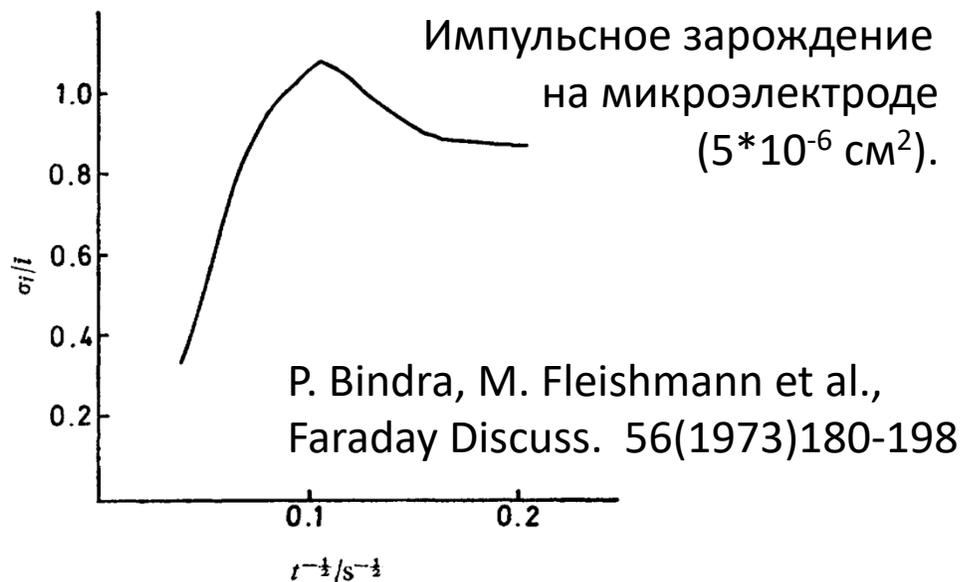
$$i = A'Bt^3/3 \text{ A cm}^{-2}$$



+ установлены условия формирования α - и β -модификаций



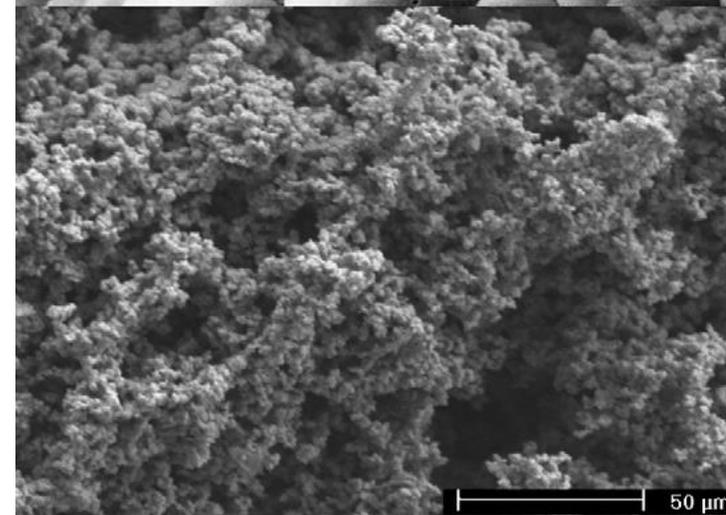
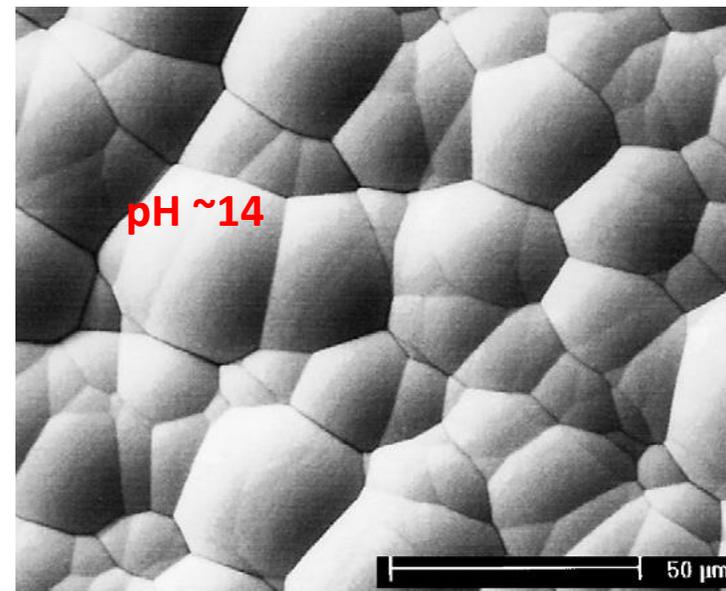
P. Perret et al., J. Electrochem. Soc. 156 (2009) A645-A651



P. Bindra, M. Fleishmann et al., Faraday Discuss. 56(1973)180-198

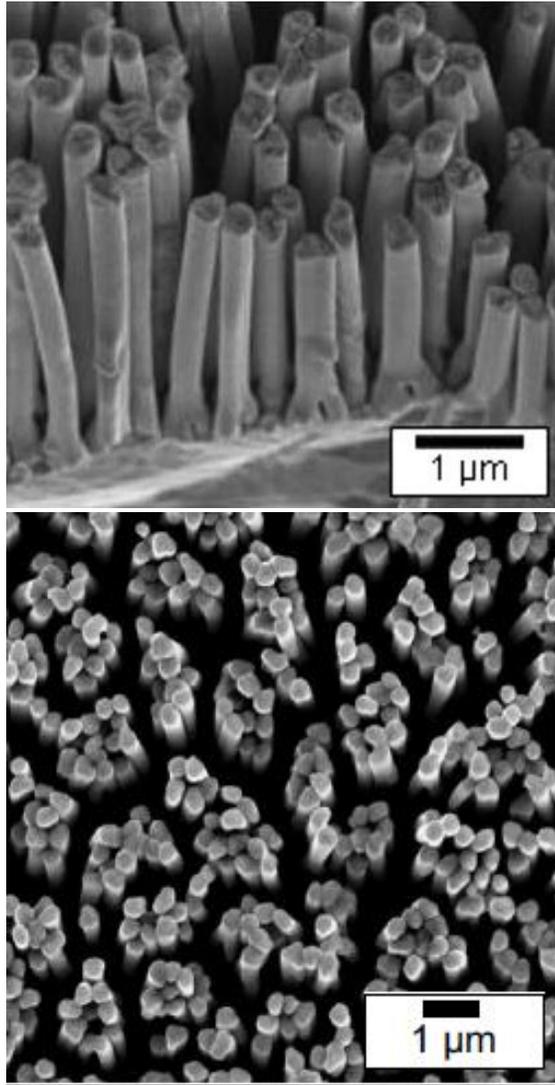
Электрофоретическое соосаждение, дополнительные центры нуклеации

ДИОКСИД СВИНЦА

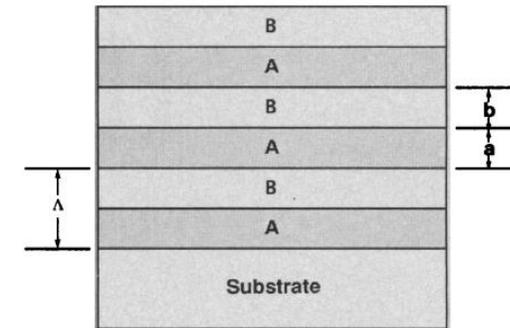
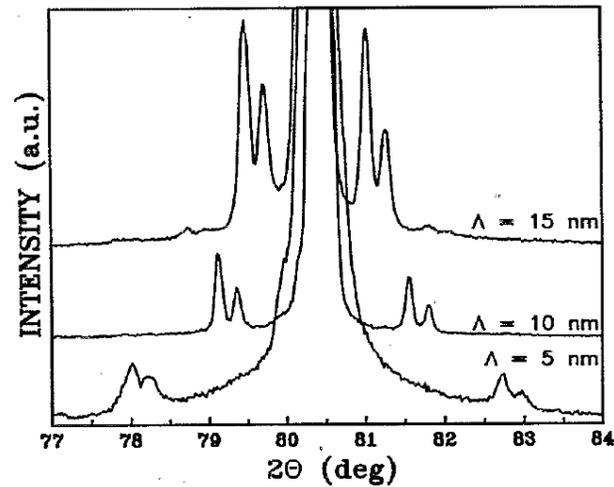
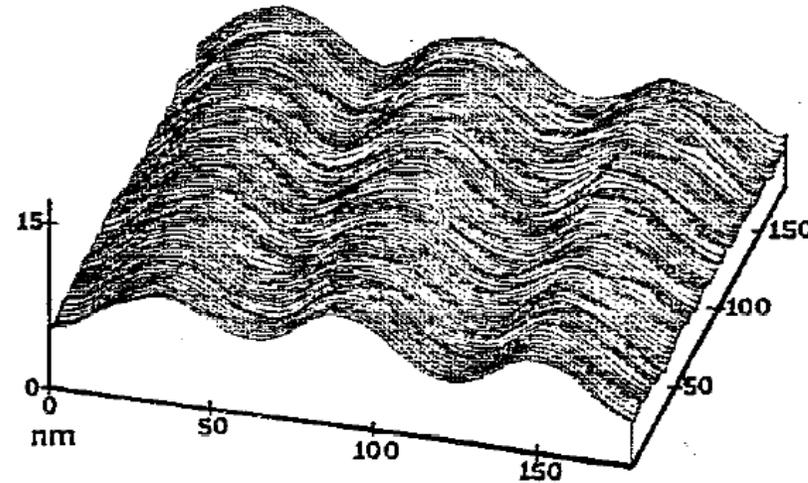


S.Cattarin, M. Musiani, Electrochim. Acta, 52 (2007) 2796-2805

Наноструктуры на основе PbO_2



P. Perret et al.,
J. Electrochem. Soc.
156 (2009) A645-A651

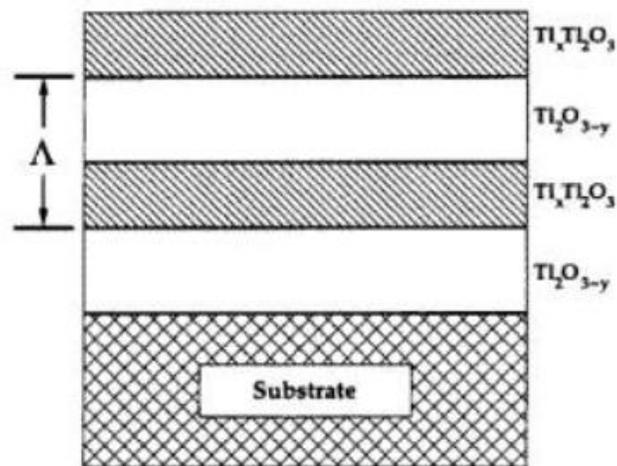
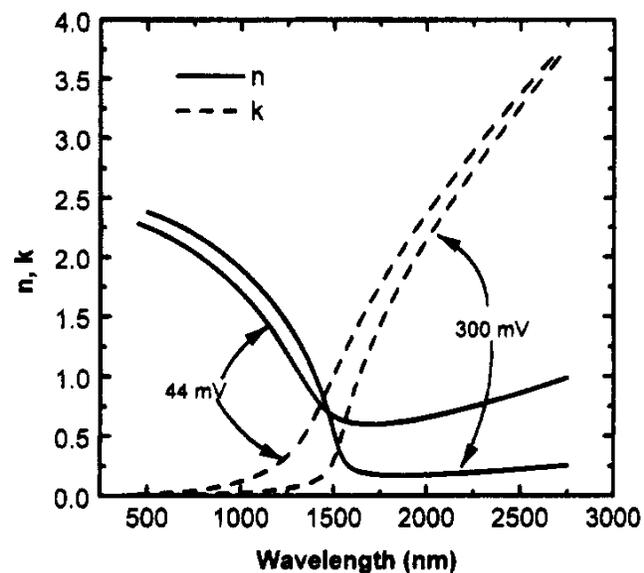


J. Switzer et al.:
Science 247 (1990) 444-446;
Appl. Phys. Lett. **63** (1993)
1501 -1503.

Optical and Electronic Transport Properties of Electrodeposited Thallium(III) Oxide Films

Robert A. Van Leeuwen, Chen-Jen Hung, Daniel R. Kammler, and Jay A. Switzer*

overpotential (mV)	carrier density ($\times 10^{20} \text{ cm}^{-3}$)	resistivity ($\mu\Omega \text{ cm}$)	mobility ($\text{cm}^2/\text{V s}$)
535	8.6	86	100
400	8.3	80	94
300	8.7	78	93
220	9.5	75	88
190	9.8	74	86
117	9.5	74	89
90	10.7	130	45
44	11.0	285	27



J. Chim. Phys., Vol. 65 (1968), pp. 2119–2125

Oxydation anodique du curium

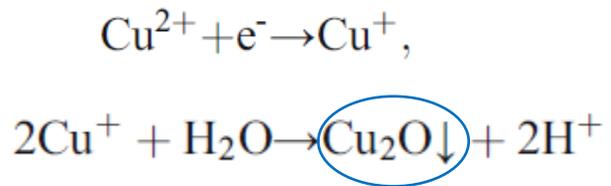
Moïse Haissinsky, Jean-Claude Dran, Roger Klein et Élisabeth Pluchet

Laboratoire Curie, 11, rue Pierre et Marie Curie, Paris, 5 e France.

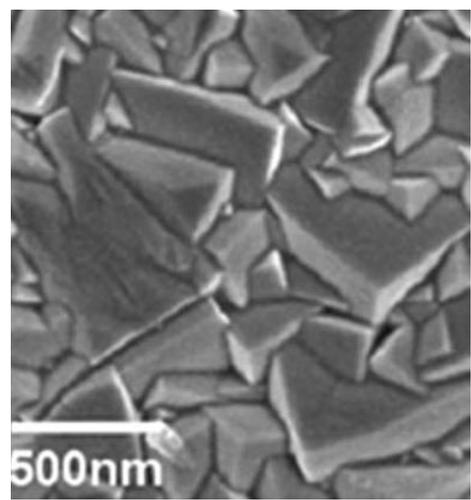
Résumé

On précise les facteurs dont dépend le dépôt anodique du curium : concentration, acidité, potentiel, nature de l'anion, agitation, etc. On a examiné le rôle d'un certain nombre de réactifs qui peuvent soit attaquer le dépôt en le portant en solution, soit le favoriser par stabilisation ou même en augmentant sa quantité. On conclut que le dépôt est constitué essentiellement par le bioxyde CmO_2 .

After the electrolysis a brown deposit was noted on the anode, containing curium. We observed the appearance of a deposit also in our previous experiments¹ at the oxidation of terbium, praseodymium, and californium: however, in the case of curium the amount of the deposit on the anode was much less. The radiometric analysis de-

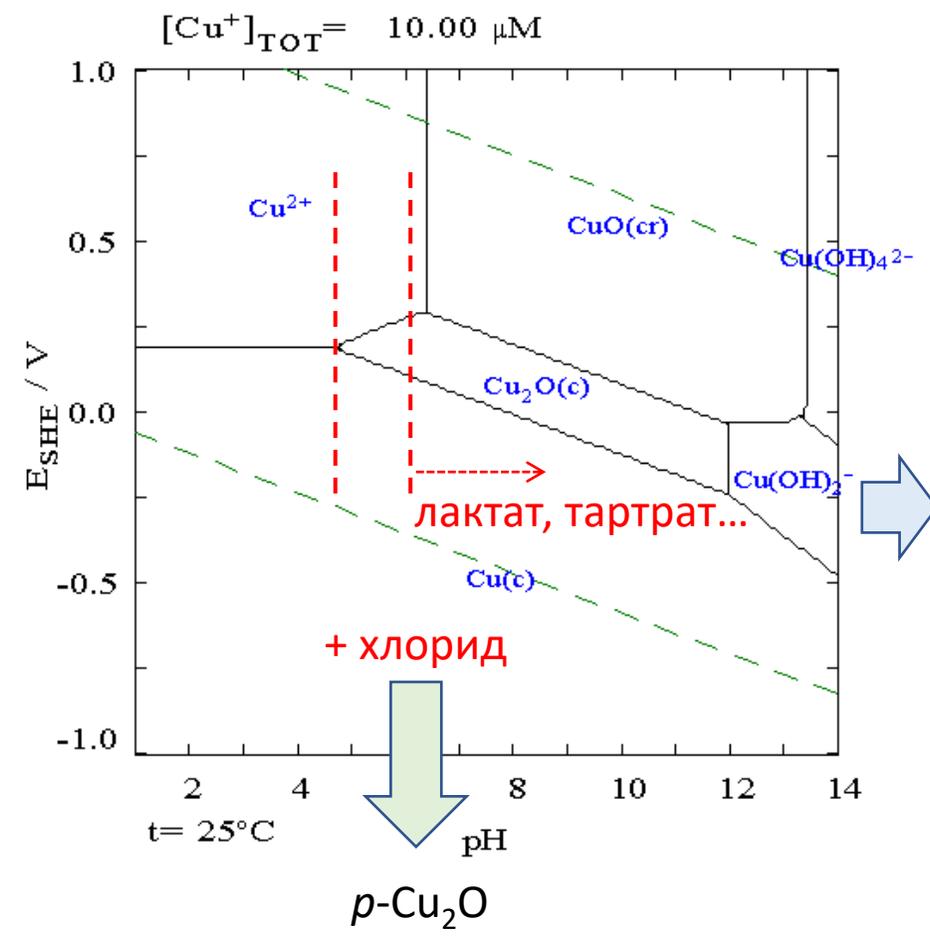


pH 11

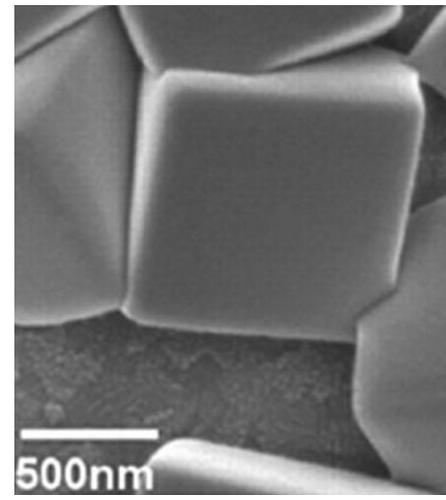


**Катодная электрокристаллизация
(оксид меди)**

C.M.McShane
et al., J. Phys.
Chem. Lett .
1 (2010) 2666–2670

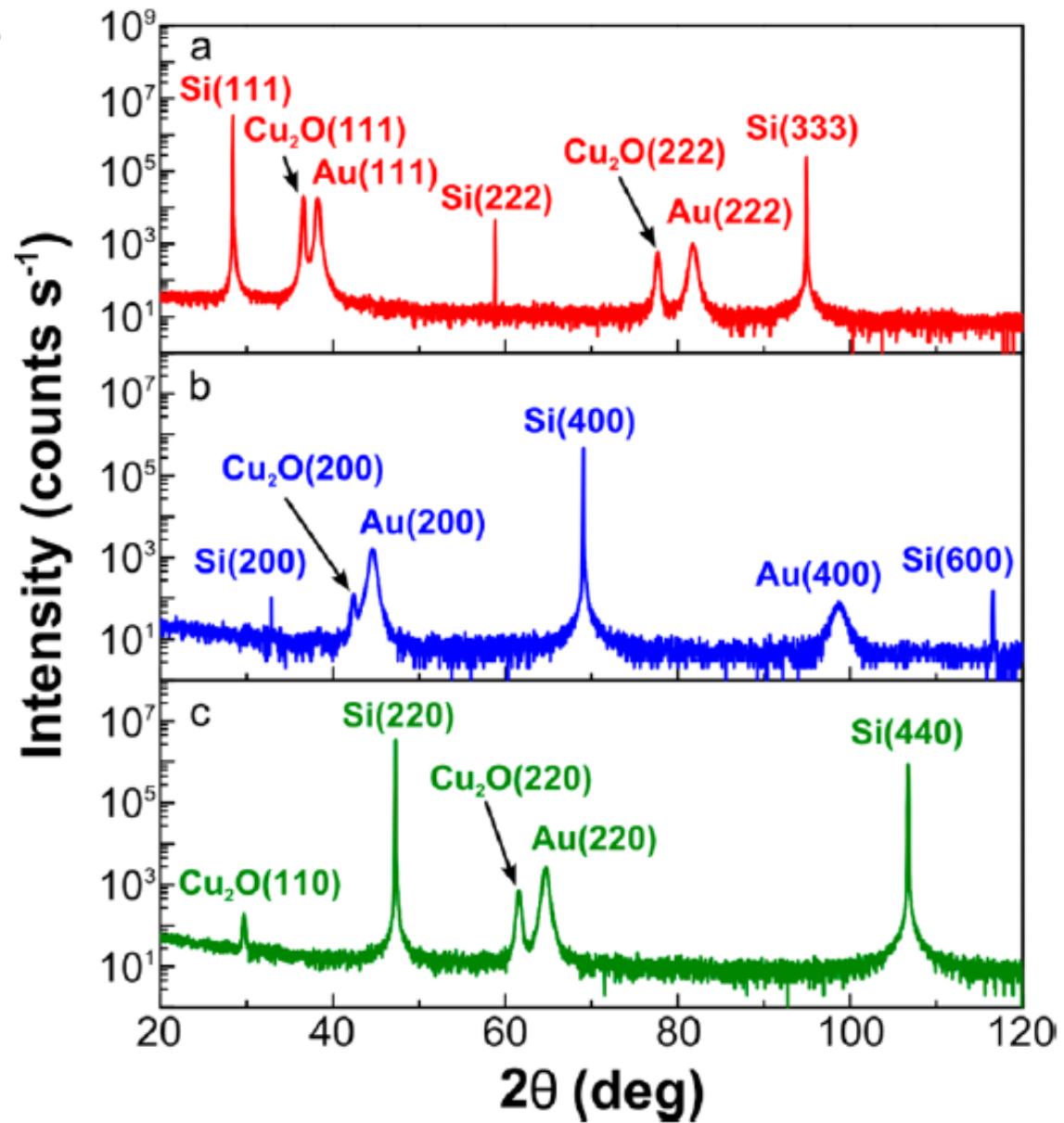
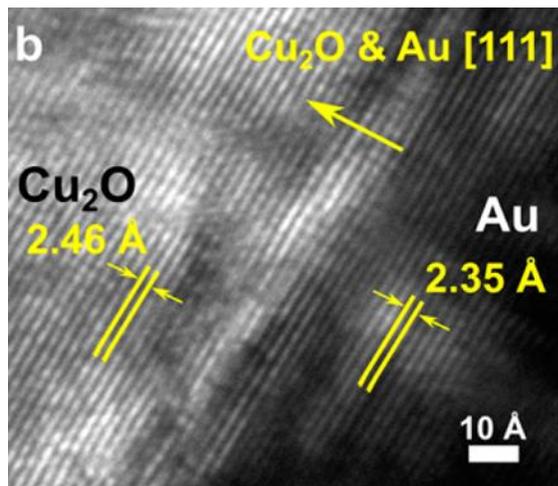
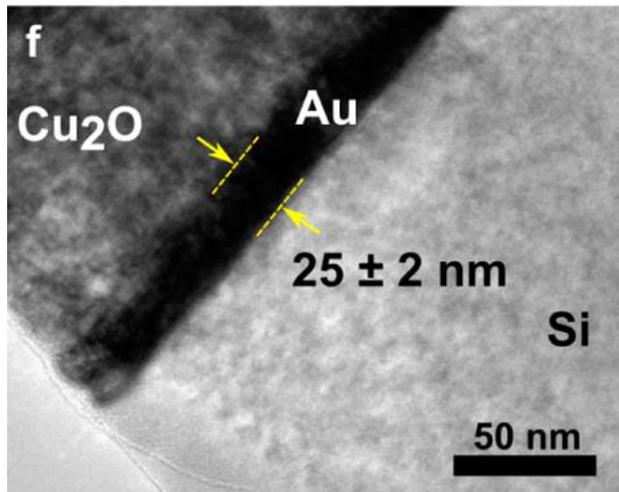


pH 13



Recent review:
I.S. Brandt et al.,
J. Solid State Electrochem.
21 (2017) 1999–2020

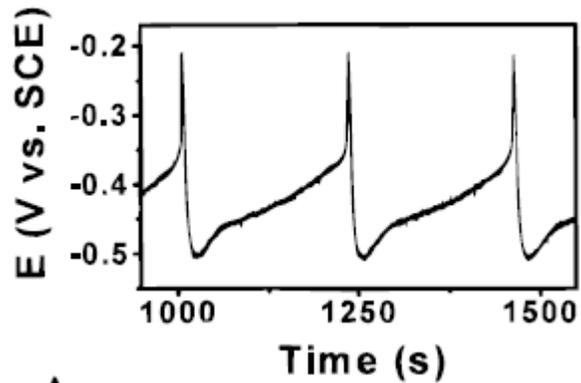
Эпитаксиальное осаждение Cu_2O (J. Switzer et al.)



J. Am. Ceram. Soc.
88 (2005) 253–270



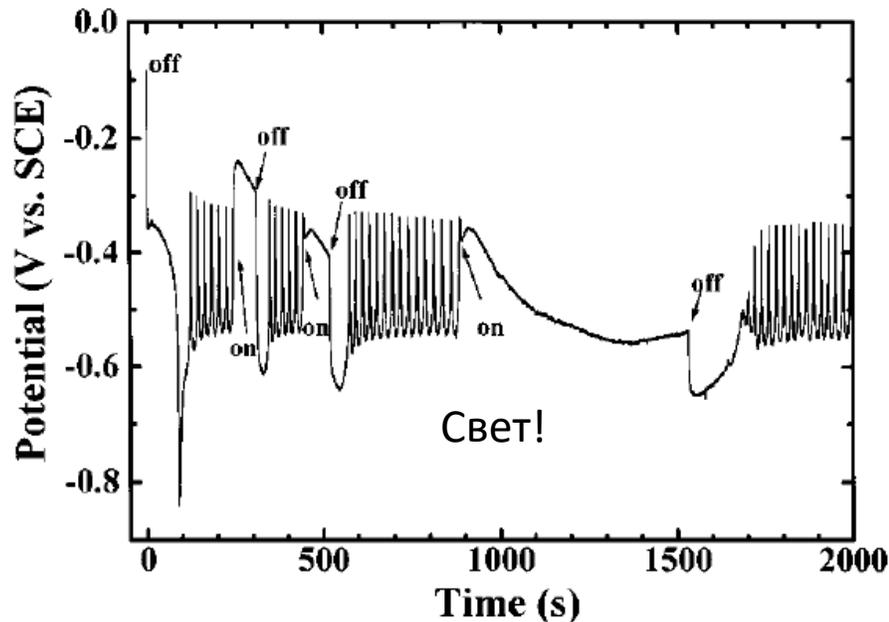
ACS Appl. Mater. Interfaces
8 (2016) 15828–15837



Самопроизвольные осцилляции потенциала при гальваностатическом осаждении



Cu₂O/Cu слоистые структуры



Наноструктуры на основе Cu₂O

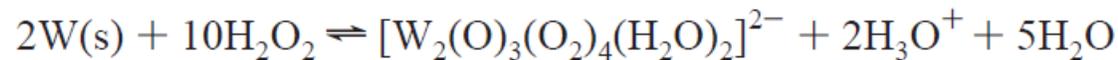


Нити Cu₂O, осаждение в ААО мембрану:

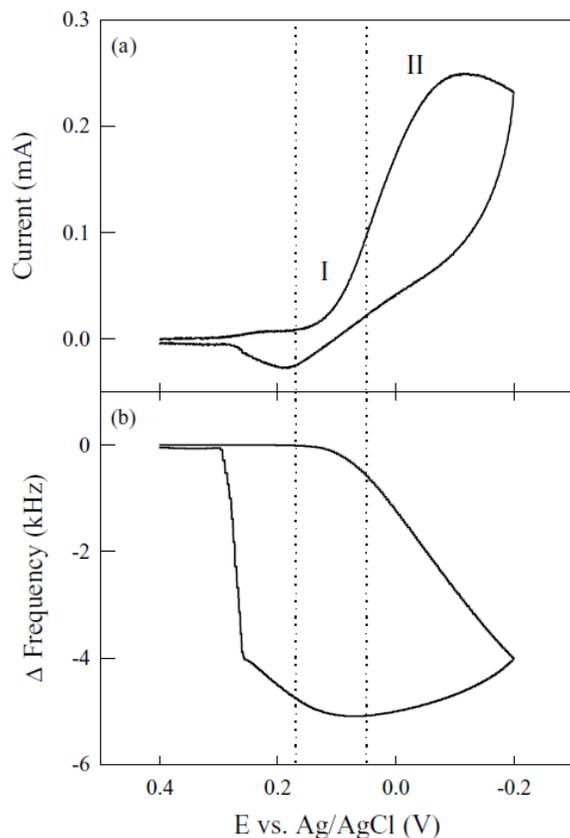
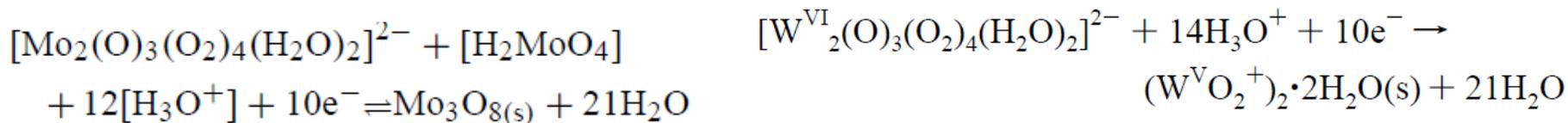
A.Jagminas et al., Appl. Surface Sci. 225 (2004) 302–308

J. Switzer et al., J. Am. Chem. Soc. 120 (1998) 3530-3531

Нестехиометрические оксиды Mo, W и V



1 - Из пероксокомплексов



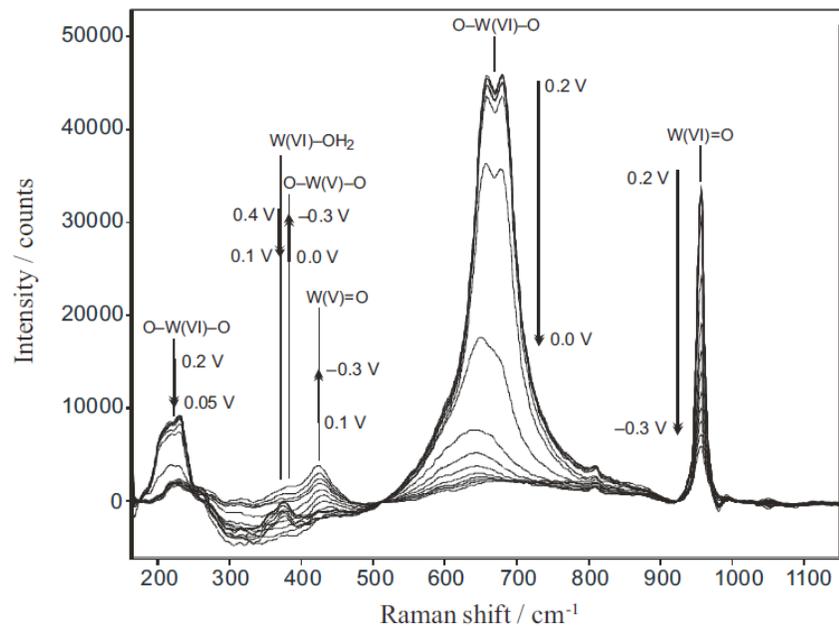
solution comp (mol %)	film comp (est by EDS)
100 W	WO ₃
10 Mo/90 W	Mo _{0.42} W _{0.58} O ₃
20 Mo/80 W	Mo _{0.55} W _{0.45} O ₃
30 Mo/70 W	Mo _{0.59} W _{0.41} O ₃
50 Mo/50 W	Mo _{0.73} W _{0.27} O ₃
100 Mo	α-/β-MoO ₃ ^b
100 Mo	α-MoO ₃
100 Mo	β-MoO ₃ ^b

T.M. McEvoy, K. J. Stevenson,
Anal. Chim. Acta 496 (2003) 39–51

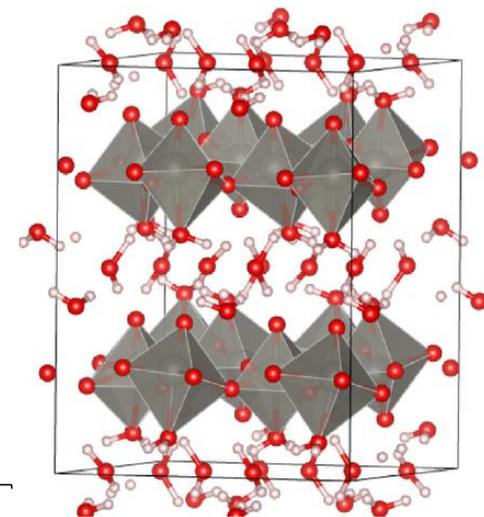
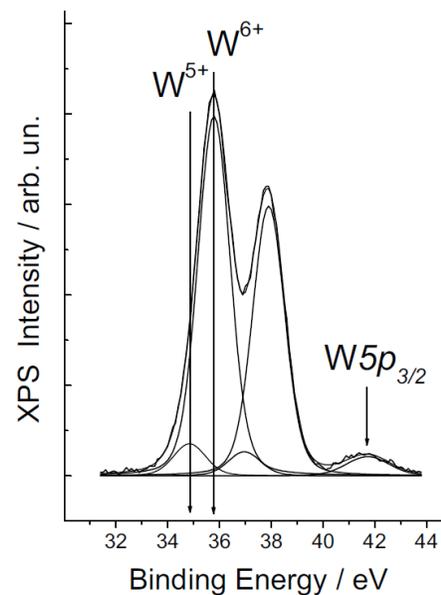
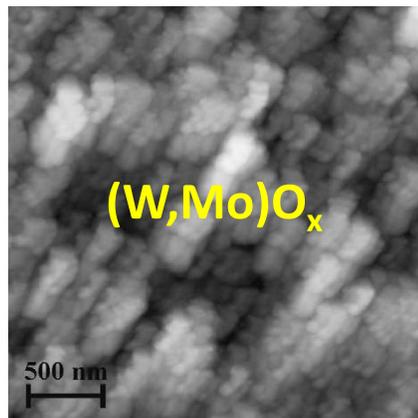
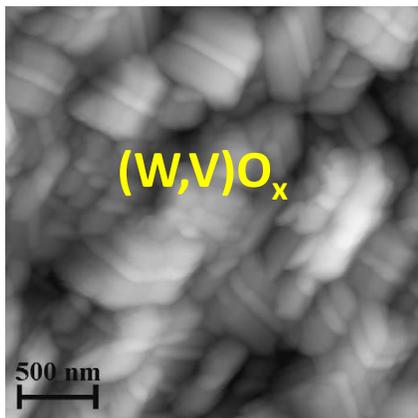
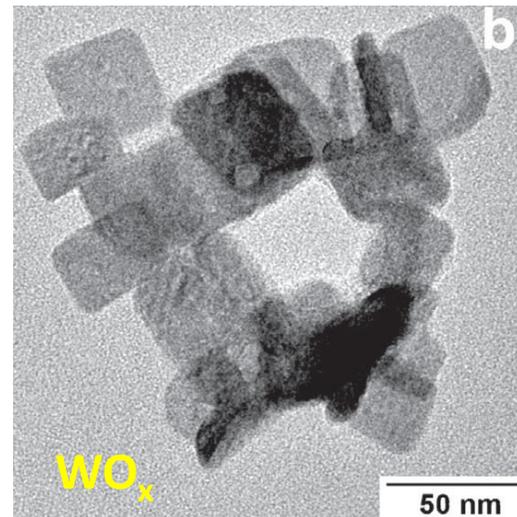
L. Kondrachova et al.,
Langmuir 22 (2006) 10490-10498

Нестехиометрические оксиды Mo, W и V

2 - из метастабильных растворов изополисоединений

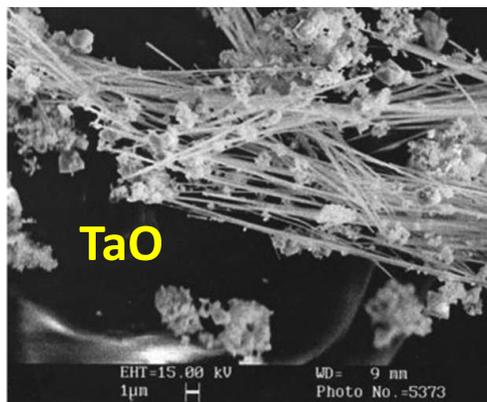


V.K. Laurinavichute,
Electrochim.Acta
54 (2009) 5439–5448
56 (2011) 3530–3536

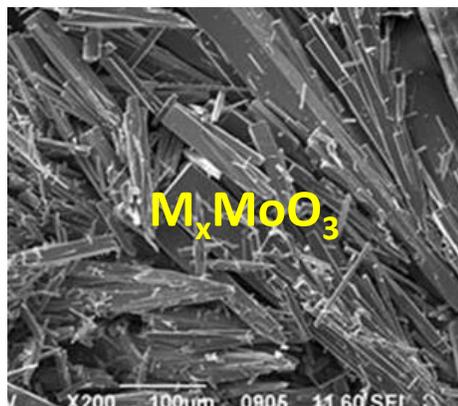


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Электрокристаллизация оксидов из расплавов

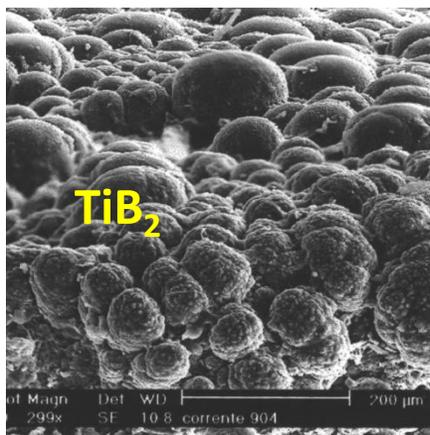


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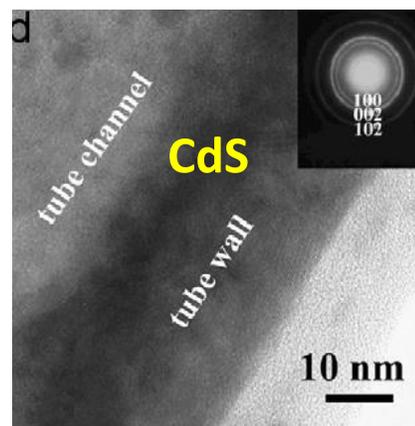


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Электрокристаллизация других бинарных соединений



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Общие вопросы

- «прекурсоры» в растворах/расплавах
- термодинамика нестехиометрических соединений
- управление природой «активных центров»

Электрохимическая интеркаляция для регулирования стехиометрии

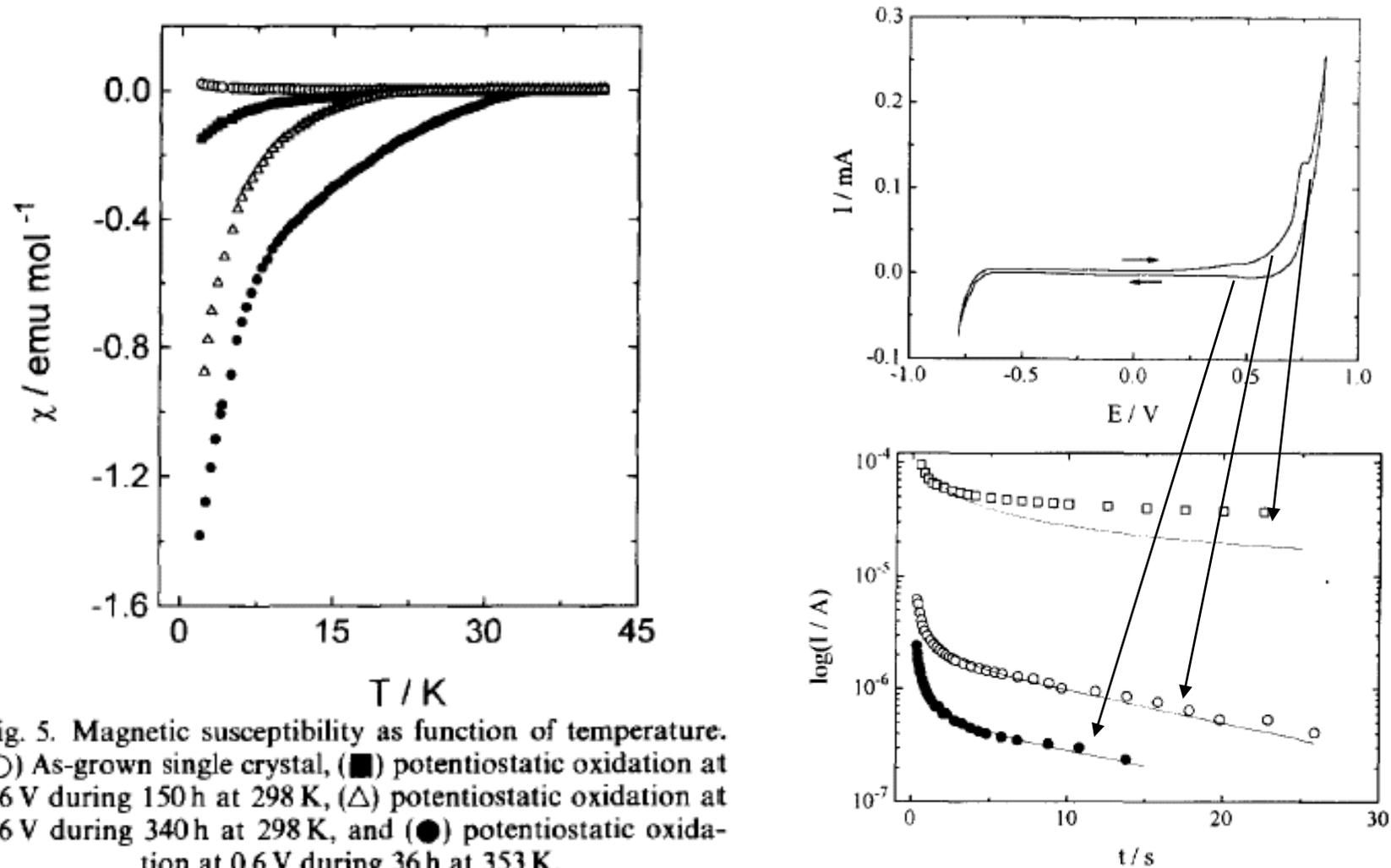
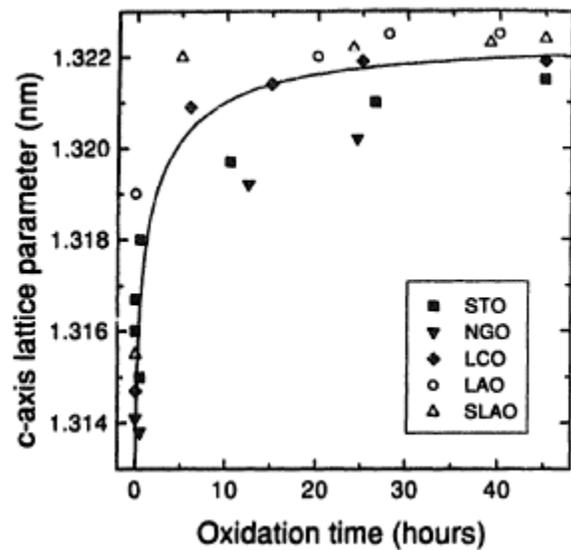
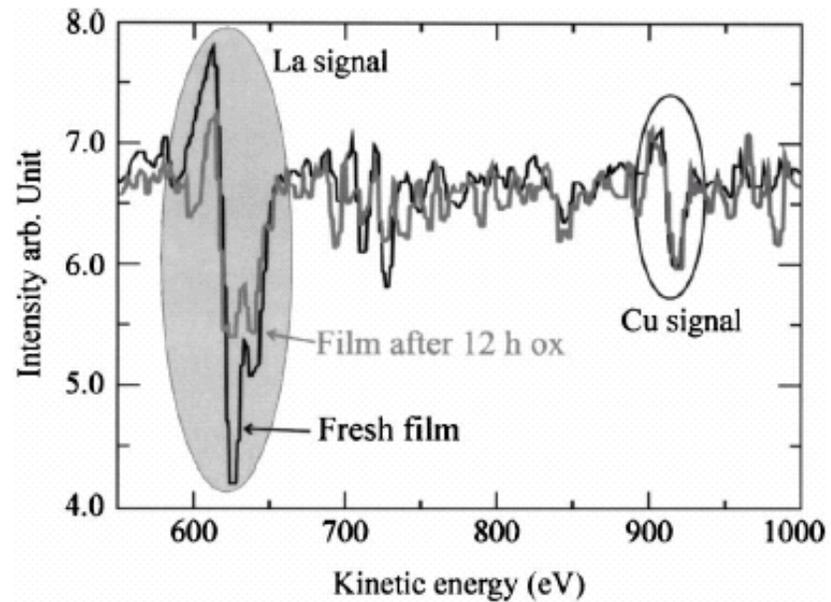
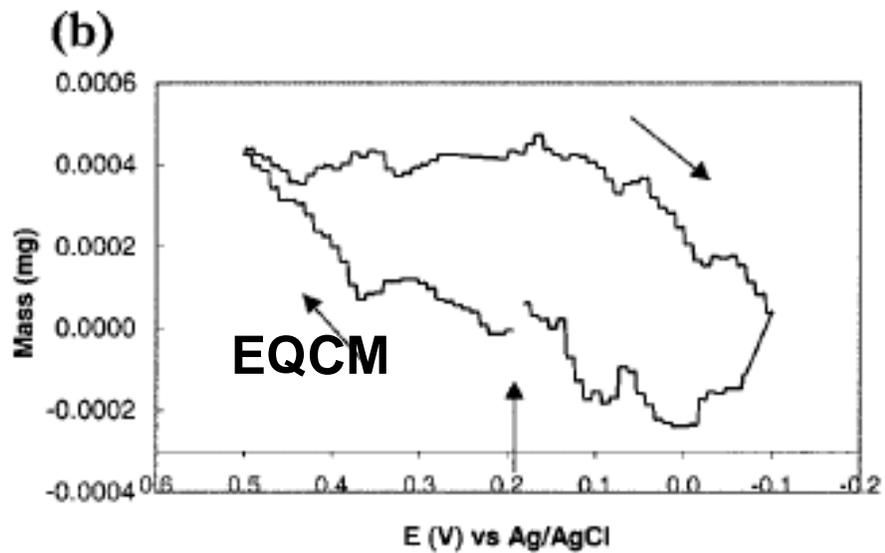
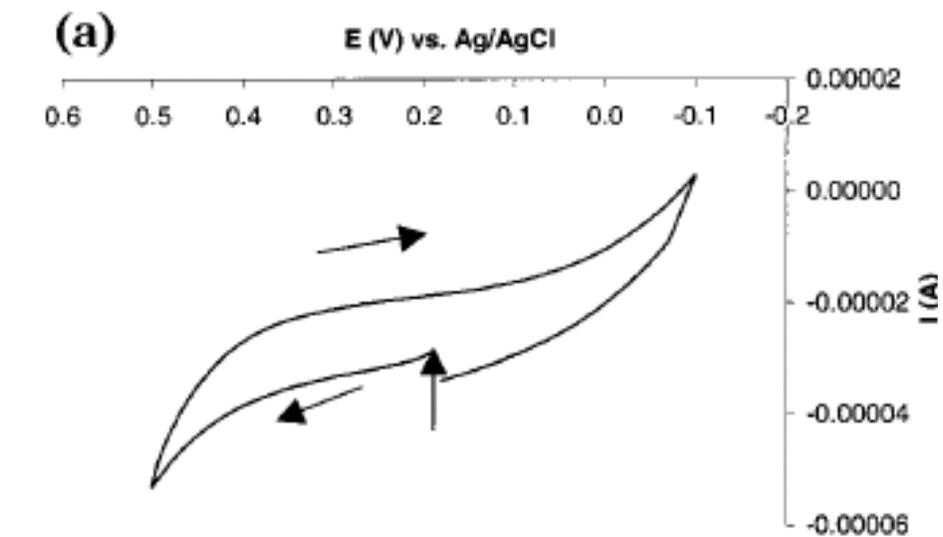
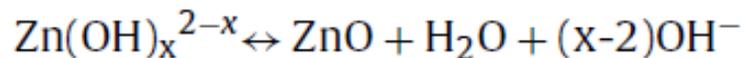
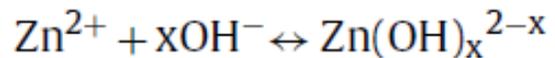
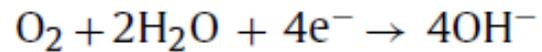


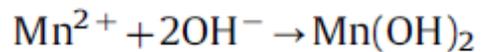
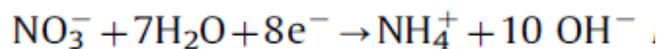
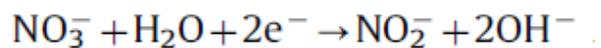
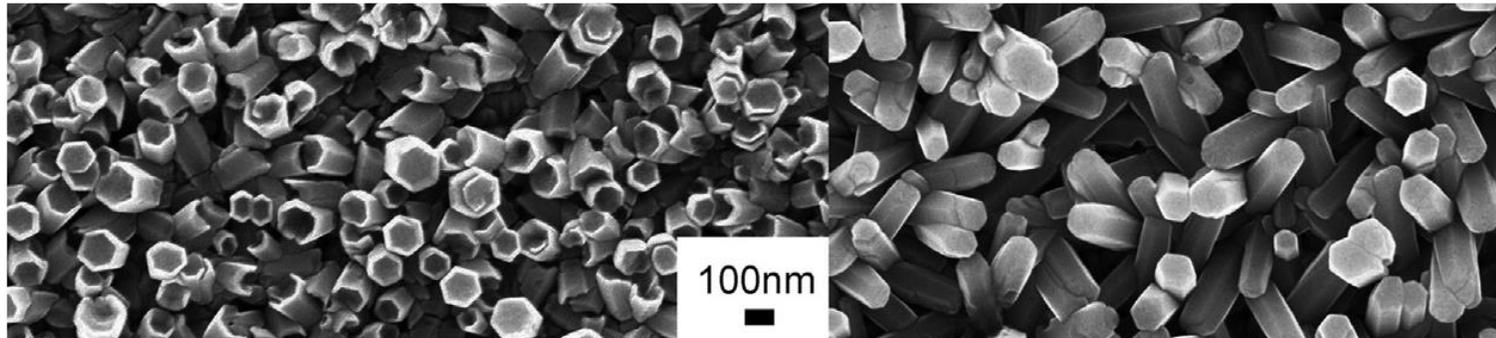
Fig. 5. Magnetic susceptibility as function of temperature. (○) As-grown single crystal, (■) potentiostatic oxidation at 0.6 V during 150 h at 298 K, (△) potentiostatic oxidation at 0.6 V during 340 h at 298 K, and (●) potentiostatic oxidation at 0.6 V during 36 h at 353 K.



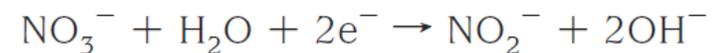
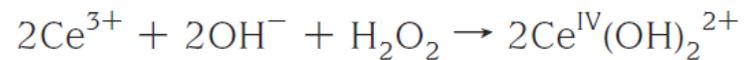
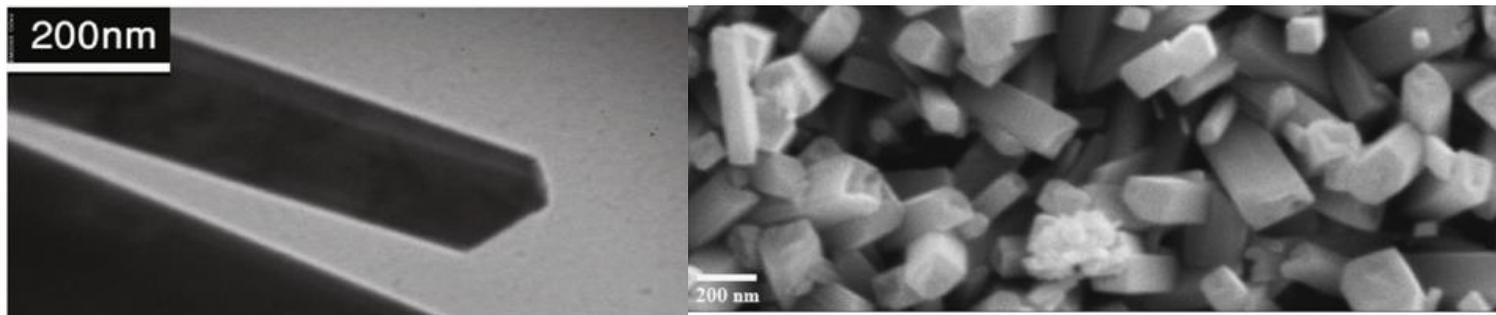
Электрохимически индуцированное осаждение



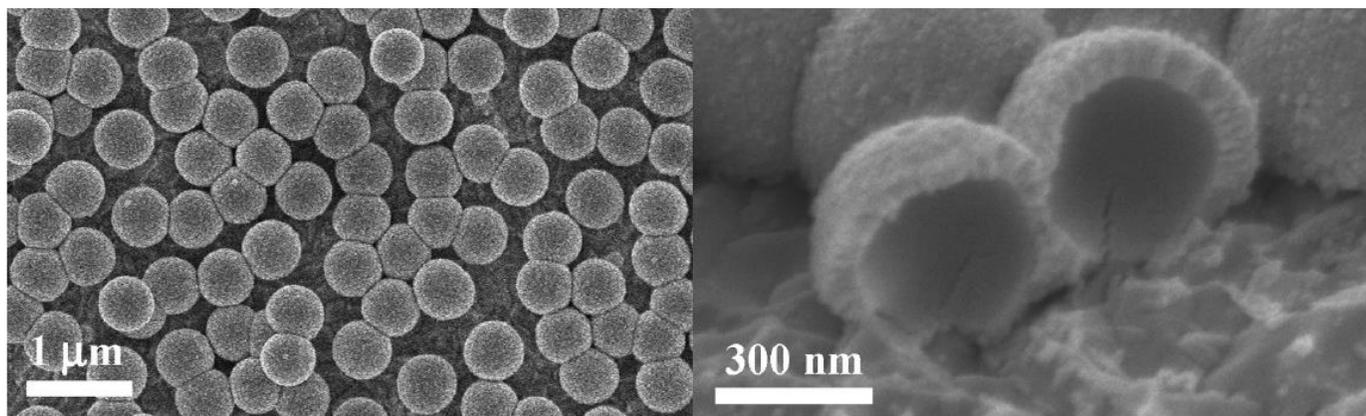
Electrochimica Acta 132 (2014) 370–376



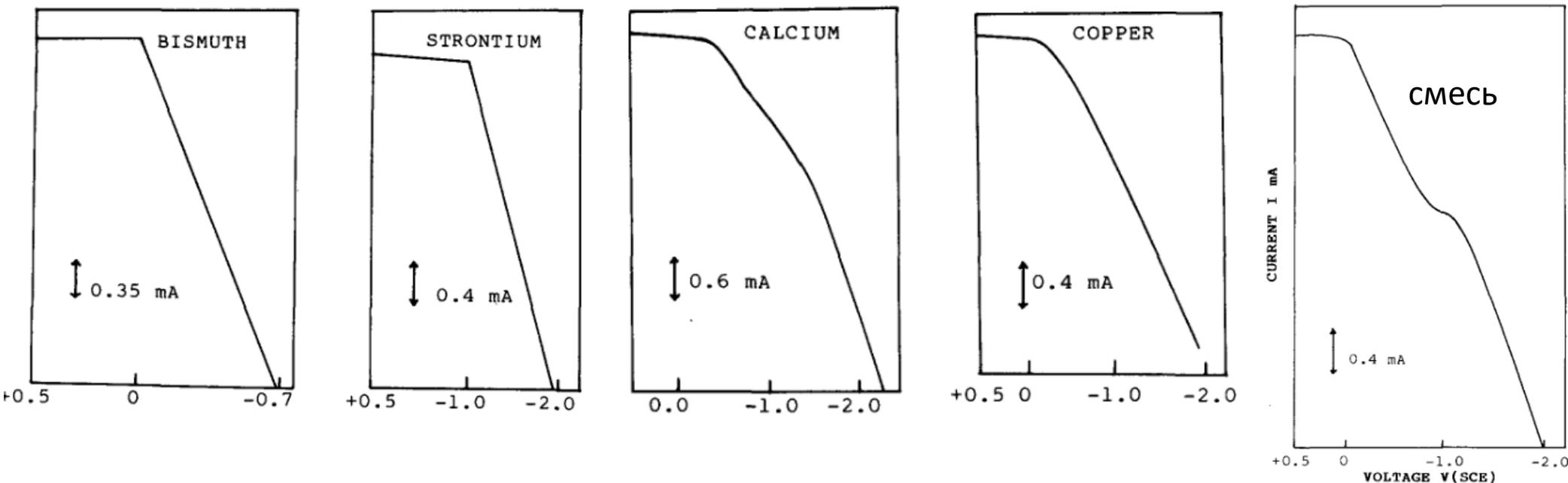
J. Solid State Chem. 190 (2012) 202–207



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Купратные сверхпроводники из смеси металлов, полученной электроосаждением из растворов в ацетоне



Mater. Res. Bull.
25 (1990) 1443-1451

Перовскиты из гидроксидов, полученных электрохимически индуцированным осаждением

Compound	% Weight loss		T/°C	Compound	Electrolyte used			Crystal system JCPDS-PDF	Cell parameters/Å		
	Expected	Observed			Ln/M	Conc./M	pH		a	b	c
LaAlO ₃	20.17	30.1	950	LaAlO ₃	0.42	0.15	2.58	Rhombohedral 31-22	5.36	-	13.11
PrAlO ₃	20.00	28.6	950	PrAlO ₃	0.33	0.15	3.15	Rhombohedral 29-76	5.33	-	12.97
NdAlO ₃	19.78	29.1	950	NdAlO ₃	0.33	0.15	2.15	Rhombohedral 39-487	5.32	-	12.91
LaFeO ₃	18.21	20.2	950	LaFeO ₃	0.66	0.15	1.95	Orthorhombic 37-1493	5.57	7.86	5.55
PrFeO ₃	18.09	19.2	950	PrFeO ₃	0.66	0.15	0.90	Orthorhombic 15-134	5.48	5.58	7.79
NdFeO ₃	17.89	20.3	950	NdFeO ₃	0.66	0.15	1.89	Orthorhombic 25-1149	5.58	7.76	5.45
PrMnO ₃	12.97	12.13	675	PrMnO ₃	0.66	0.15	1.10	Pseudocubic	3.87	-	-
NdMnO ₃	12.81	13.41	675	NdMnO ₃	0.66	0.15	2.23	Pseudocubic	3.86	-	-
LaCoO ₃	27.0	27.5	950	LaCoO ₃	0.66	0.2	2.68	Rhombohedral 25-1060	5.44	-	13.08
LaNiO ₃	-	-	550	LaNiO ₃	0.66	0.2	2.45	Rhombohedral 34-1181	5.45	-	6.56