CHEMICALS FOR VAPOR AND ATOMIC LAYER DEPOSITION

NNCI ALD/MOCVD Symposium Harvard University October 4th, 2019



COMPANY HISTORY & BACKGROUND

- 1964 company founded, manufacturing in Danvers, MA
- 1978 moved corporate HQ to Newburyport, MA
- 1986 established European HQ in Strasbourg, France
- 2014 Strem celebrated its
 50th year anniversary
- Global network of distributors
 - Europe, Asia, Middle East

- 5,000 Specialty Chemicals for Research & Production
- Custom Synthesis and cGMP Manufacturing
- World-wide customer base



Company Strategy: Provide specialty chemicals of high quality, in a timely fashion



HUMAN RESOURCES

- Small company with ~78 employees
- many employees at company over 10 years, low turnover
- > 14 employees are Ph.D.'s
- Approximately 1/4 each in manufacturing, customer service, warehouse, administrative/facility
- In 2006 Strem implemented an ESOP (Employee Stock Ownership Program), making all employees partial owners of Strem





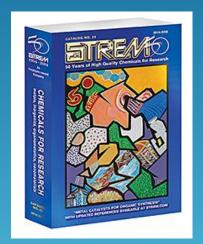
ENVIRONMENTAL, HEALTH, SAFETY + SECURITY (EHS+S)

- Strem is a member of SOCMA (Society of Chemical Manufacturer's and Affiliates)
- Safety is of primary importance
- Strem subscribes to SOCMA's EHS+S program
- Regular training of staff, internal and external audits
- First Responders trained from lab and warehouse
- 2012-2019 Gold, Silver and Bronze Performance Improvement Awards from SOCMA for outstanding commitment to continuous improvement in EHS&S practices.
- ISO 9001:2015 certified CERTIF

em Chemicals



PRODUCT & MARKETS SERVED



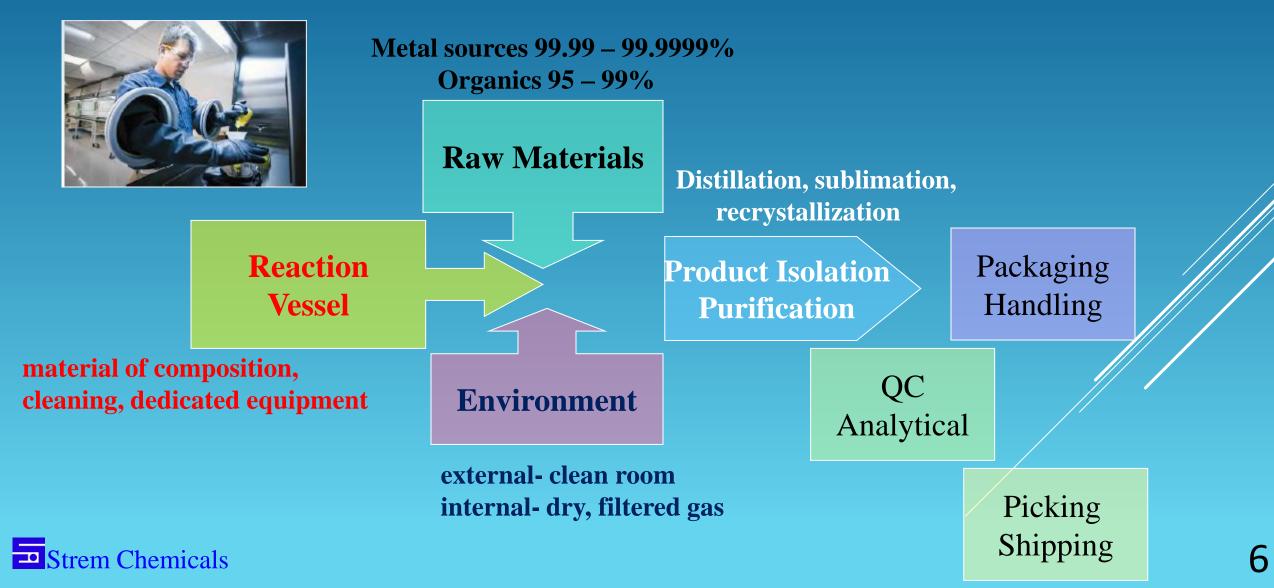




Customer base is global

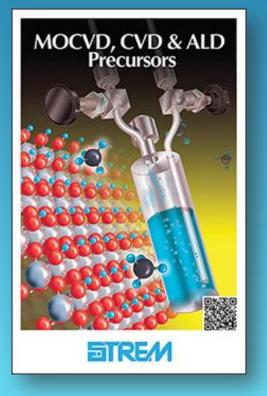
HOW STREM BUILDS IN HIGH QUALITY:

High Quality is built into the product at each step



MORE THAN 450 METAL PRECURSORS FOR CVD, ALD

Strem has a broad range of CVD/ALD precursors



Metal alkyls
 Metal alkylamides and alkylimides
 Metal Amidinates
 Volatile metal carbonyls
 Metal alkoxides
 Metal betadiketonates (and ligands
 Volatile organometallics, MetalCps

Metal Halides

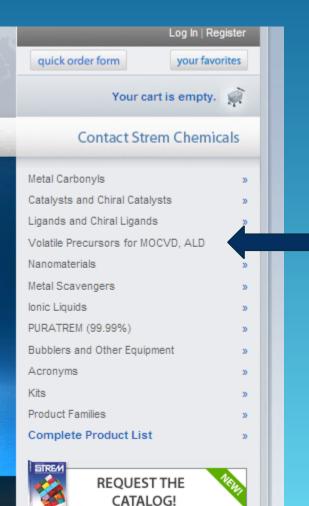
Metals Purity - 99,99% and higher

High Purity Inorganics

Strem Chemicals

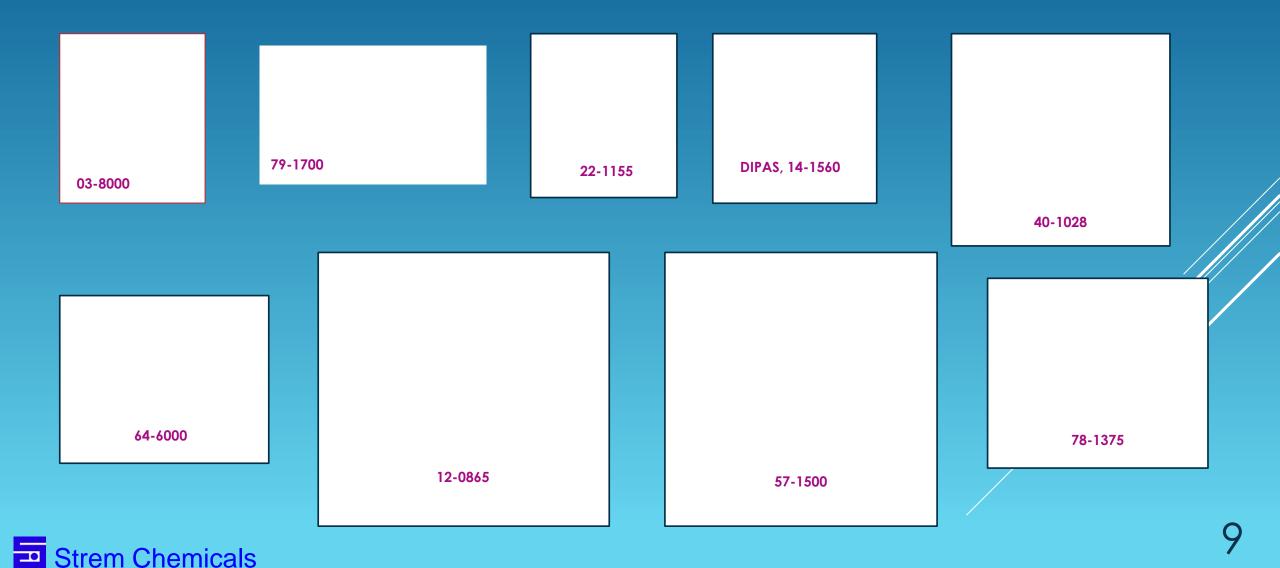
VOLATILE PRECURSORS FOR CVD, ALD ON STREM WEBSITE





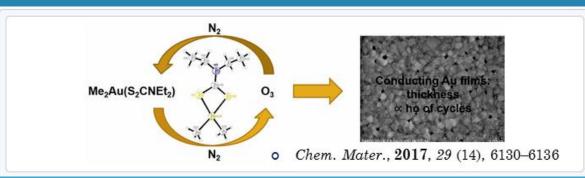
D Strem Chemicals

New products for ALD/CVD (2018-2019)



Gold ALD/CVD Precursor

- Volatile, air, light and thermally stable precursor
- 79-1700,(N,N-Diethyldithiocarbamato)dimethylgold(III), 97% (99.999%-Au) PURATREM



Thermal Atomic Layer Deposition of Continuous and Highly Conducting Gold Thin Films

University of Helsinki

- o 1. Chem. Mater., 2017, 29 (14), 6130–6136
- o 2. Journal of Crystal Growth 2015, 414, 143-150
- o 3. Physics Procedia 2013, 46, 167-173
- 4. Gold Bulletin (Berlin, Germany) 2011, 44(3), 177-184



NEW PRODUCTS IN DEVELOPMENT; STREM # 44-5150 AND 78-0550.

Focused electron beam-induced deposition precursor for Ru and Pt;

Allylruthenium(II) tricarbonyl bromide

Lisa McElwee-White, University of Florida

Volatile material, sublimes at room temperature at 100 mTorr.

Cis-Dichlorodicarbonylplatinum(II).

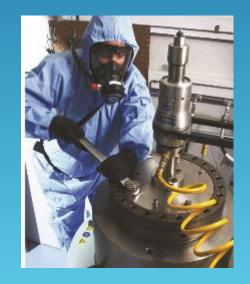
Used for focused electron beam induced deposition of Pt

44-5150

HIGH PRESSURE CAPABILITIES AT STREM CHEMICALS – METAL CARBONYLS

In 1964, Strem Chemicals, Inc. began manufacturing metal carbonyls and metal carbonyl derivatives utilizing two, stainless steel, high pressure reactors



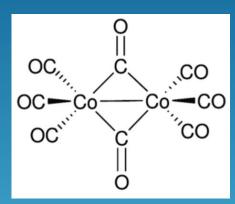


12

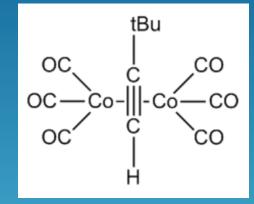
27-0400, Cobalt carbonyl (Dicobalt octacarbonyl)



CCTBA IS USED FOR COBALT DEPOSITION COBALT CARBONYL IS THE PRECURSOR



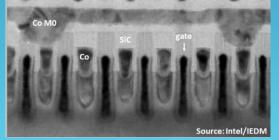
Dicobalt Octacarbonyl Strem 27-0400



CCTBA Strem 27-0770



Strem Chemicals



http://semimd.com/chipworks/2017/12/18/ iedm-2017-intels-10nm-platform-process/



13

	M	et	al	A	lky	/ls			CH₃	CH ₂ '	A	S CH ₂ C	CH ₂ (H ₃	CH₃			
Η																	He
Li	Be											В	С	Ν	0	F	Ne
Na	Mg											Al	Si	Р	S	Cl	Ar
Κ	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	Ι	Xe
Cs	Ba	La	Hf	Та	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Ро	As	Rn
				Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
				Th	Pa	U											



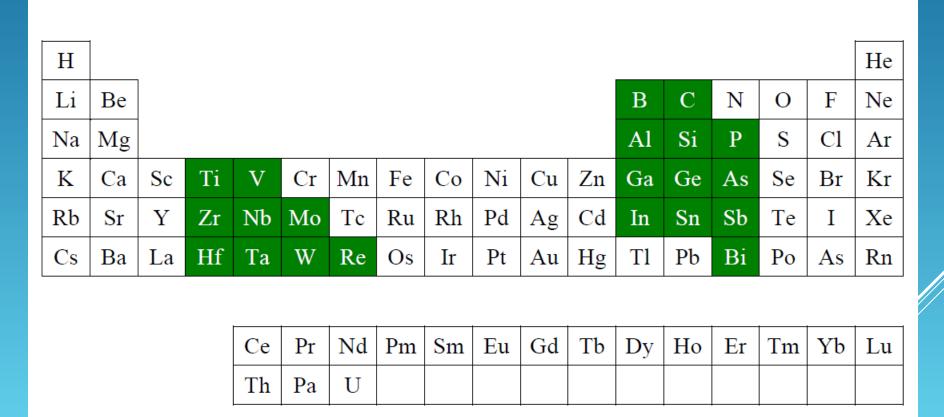
A	lk	yl	Ar	ni	de	S		H₃C	C⊦ N 7*	l ₃							
							H ₃ C~	<u>N</u>	- '	N-CH							
Η		_					H ₃ C	H ₃ C	СН	-	•						He
Li	Be									5		В	С	Ν	0	F	Ne
Na	Mg											Al	Si	Р	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	Ι	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	T1	Pb	Bi	Ро	As	Rn

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
Th	Pa	U											

N	/le	ta	ΙΑ	۱k	ОХ	id	es			Et D							
								E	tO-N	lp lp	DEt						
Η									(()	DEt						He
Li	Be									Et		В	С	Ν	Ο	F	Ne
Na	Mg											Al	Si	Р	S	Cl	Ar
Κ	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	Ι	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	T1	Pb	Bi	Ро	As	Rn
				Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
				Th	Pa	U											



Metal Halides





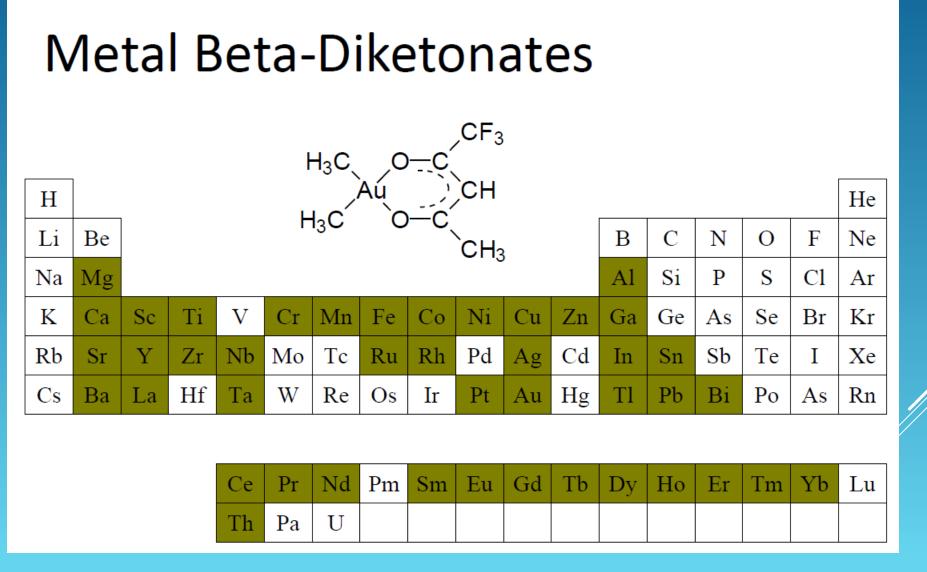
V	ola C	ati ar	_		_		I	00	JN	/	;0						
Η		_						oC	·	` `	ò						He
Li	Be								Č)		В	С	Ν	0	F	Ne
Na	Mg				-							Al	Si	Р	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	Ι	Xe
Cs	Ba	La	Hf	Та	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Ро	As	Rn
				[
				Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu

Th

Ра

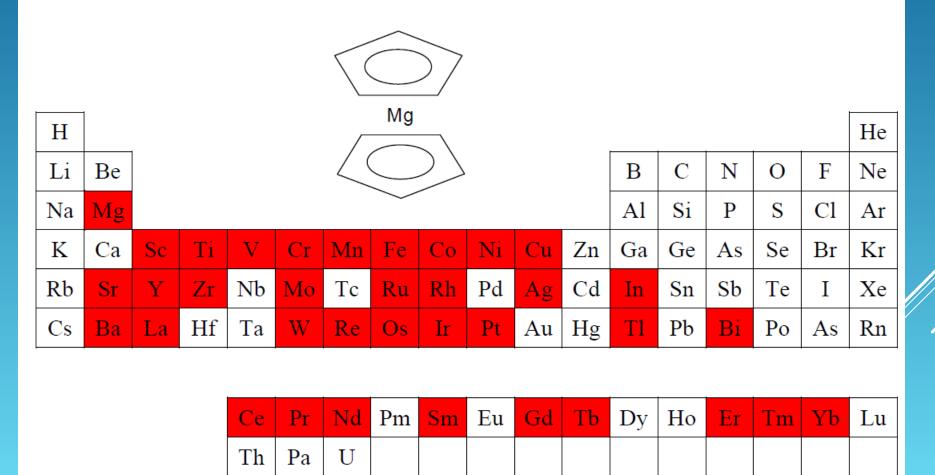
U





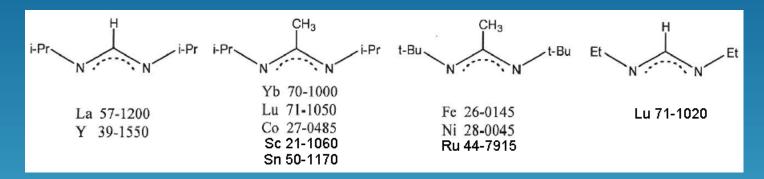


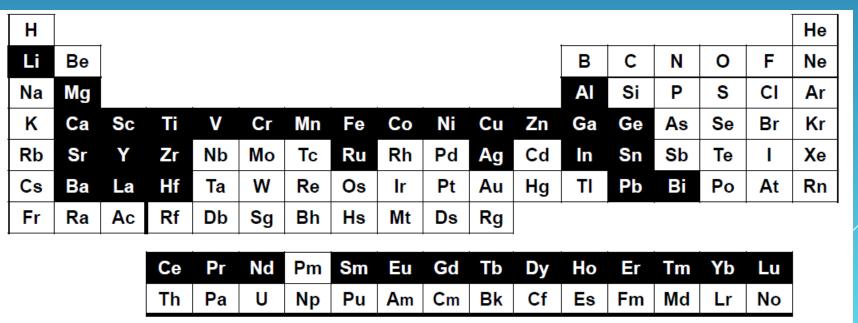
Volatile Organometallics





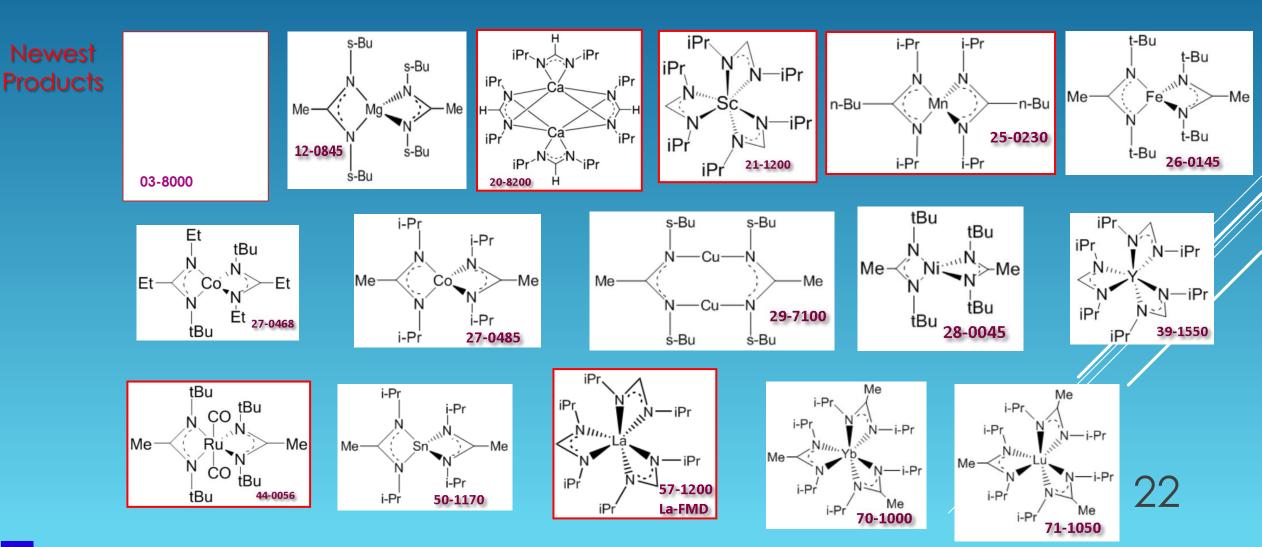
Metal Amidinates







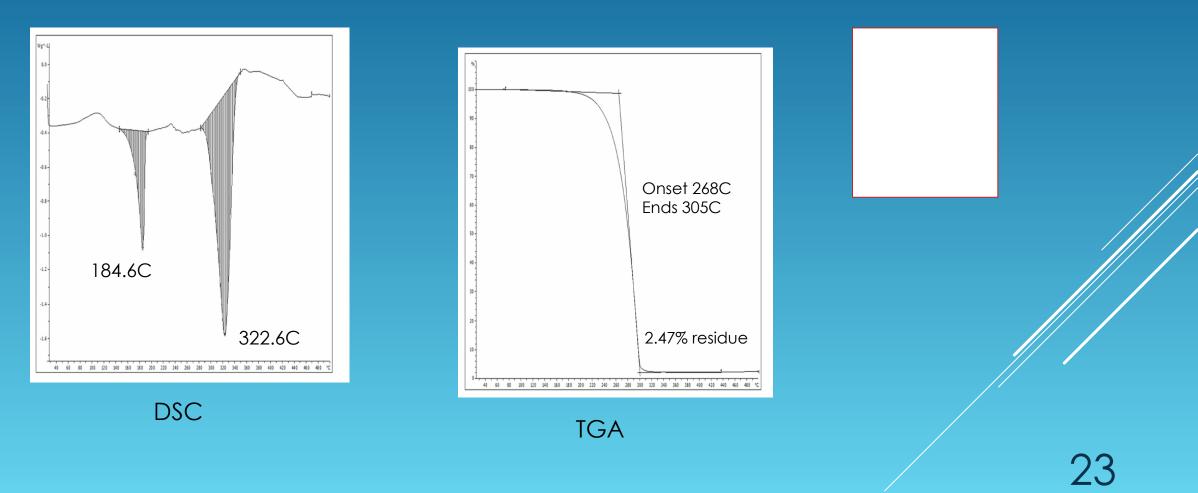
PATENTED METAL AMIDINATES



Strem Chemicals

STREM # 03-8000

(N,N-Di-i-propylacetamidinato)lithium, min. 97% (99.99+%-Li) PURATREM





STREM# 27-0485

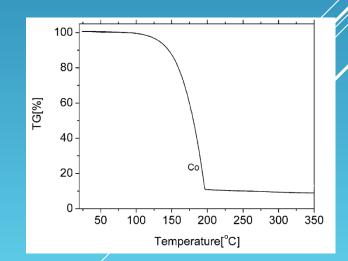
Bis(N,N'-di-i-propylacetamidinato)cobalt(II), min. 98% Co(iPr-MeAMD)2

STREM# 27-0486

Bis(N,N'-di-i-propylacetamidinato)cobalt(II), min. 98% (99.99%-Co) PURATREM (Co(iPr-MeAMD)2)

ALD precursor

- Deposition of cobalt thin films on ALD WN as a glue layer for copper interconnects in microand nanoelectronics
- High thermal stability at deposition temperature (350°C)
- Low TGA residual mass: 9%
- > Highly air and moisture sensitive





RECRYSTALIZATION



SUBLIMATION



D Strem Chemicals

STREM# 27-0485

Technical Note Safety Data Sheet Product Detail 635680-58-9 CAS Number: MDL Number: MFCD08459350 C₁₆H₃₄CoN₄ Molecular Formula: Formula Weight: 341.40 (C₈H₁₇N₂)₂Co Chemical Formula: green xtl. Color and Form: Product sold under, use subject to, terms Note: and conditions of label license at www.strem.com/harvard2.

Stability: air sensitive, moisture sensitive

Physical Characteristics: melting point 84°C, boiling point sublimes 50°C (50 mTorr)





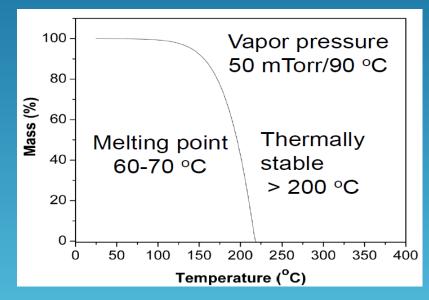
25



Bis(N,N'-diisopropylpentylamidinato)manganese(II)

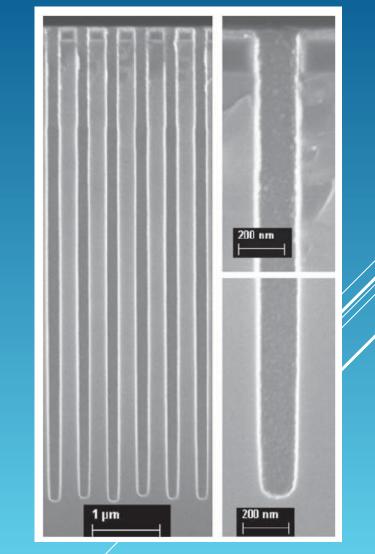
High thermal stability

Strem Chemicals



Roy Gordon's Powerpoint

Superior step coverage of Mn₄N films in holes with aspect ratios 52:1.



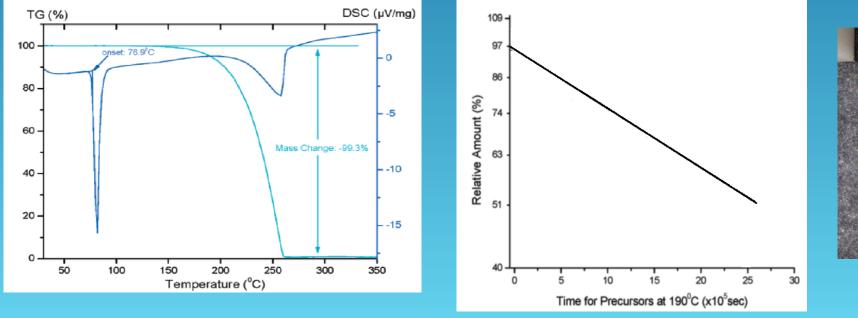
26

STREM# 29-7100

Bis(N,N'-di-sec-butylacetamidinato)dicopper(I), 99%

- Extremely low TGA residual mass: 0.7% (Negligible decomposition happened during melting and evaporation)
- High thermal stability:

Very stable even at 190°C (Typical substrate temperature for ALD of copper using these precursors.)





D Strem Chemicals

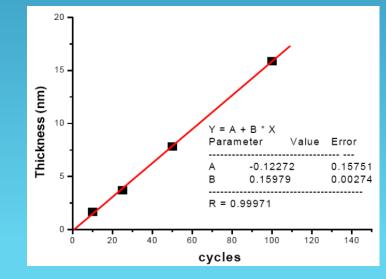
Inorg. Chem., 2005, 44, 1728-1735.

STREM# 57-1200

TRIS(N,N'-DI-I-PROPYLFORMAMIDINATO)LANTHANUM(III), (99.999+%-LA) PURATREM LA-FMD

Roy Gordon's Group

Volatile ALD lanthanum compound. (60 mTorr at 100°C)
 High reactivity to H₂O, O₂ and NH₃
 Line starts at origin => No delay in Nucleation



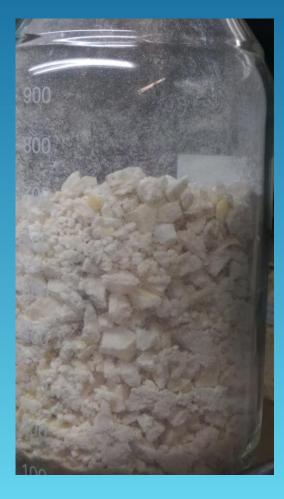


STREM# 57-1200

Product Catalog

57-1200 Lanthanum > Tris(N,N'-di-i-propylformamidinato)lanthanum(III), (99.9

Product Detail	Technical Note	Safety Data Sheet
CAS Number:	1034537-36-4	
MDL Number:	MFCD2841166	3
Molecular Formula:	C ₂₁ H ₄₅ LaN ₆	
Formula Weight:	520.53	
Chemical Formula:	C ₂₁ H ₄₅ LaN ₆	
Color and Form:	white to off-white	e pwdr.
Note:		der, use subject to, terms of label license at n/harvard2.
Stability: air sensitive,	moisture sensitive	
Safety: Hazardous - an apply	additional Dangerous Go	ods freight charge may







Strem Chemicals

Bubblers for MOCVD, CVD

CVD Bubblers (150 – 1000+ml)



ALD Cylinders



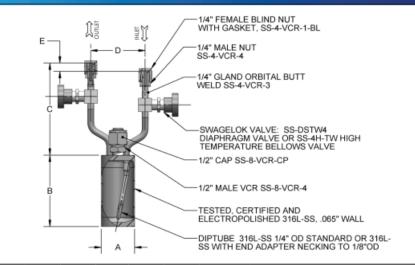
ALD CYLINDERS (50ML)



CVD BUBBLERS

Stainless Steel Bubblers: Vertical Electropolished (DOT 4B, UN stamped)

METALS • INORGANICS • ORGANOMETALLICS • CATALYSTS • LIGANDS • NANOMATERIALS • CUSTOM SYNTHESIS • CGMP FACILITIES



Stainless S	tainless Steel Bubblers, vertical, electropolished with fill-port, PCTFE valve stem tip (121°C), DOT 4B, UN stamped													
Catalog #	Vol. (mL)	A mm	B mm	C mm	D mm	E mm	Temp. Valve	Special Configuration						
95-4151	150	51	108	143	83	13	Standard							
95-4290	300	51	187	143	83	13	Standard							
95-4598	600	76	164	143	83	13	Standard							
95-4998	1000	76	254	143	83	13	Standard							
95-5002	1200	102	184	143	83	13	Standard							
95-5003	1500	102	223	143	83	13	Standard							
95-5001	2000	102	292	143	83	13	Standard							
95-5011	3000	152	213	140	83	13	Standard							
95-3000	150	51	108	140	83	13	Standard	replaceable-seat valves with rotated handles						
95-4153	150	51	108	143	83	13	Standard	with rotated handles						

31 5 Strem Chemicals

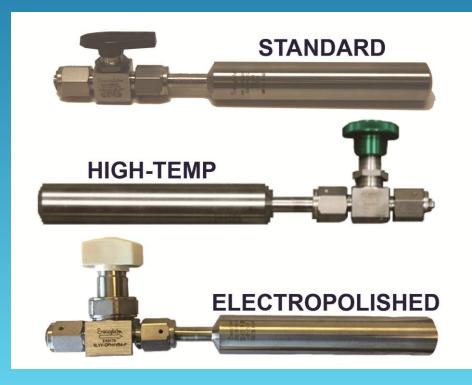
https://www.strem.com/uploads/resources/documents/electropolished_stainless_steel_bubblers

_.pdf

-0



We offer a variety of precursors prepackaged in 50mL Swagelok® Cylinders.







SERVICES OFFERED

- Filling, refilling & cleaning services
- "Request to Fill/Refill Bubbler or Cylinder" form





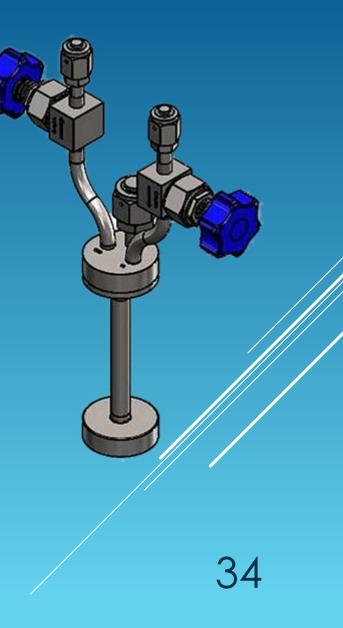






97-7000

7ML BUBBLER FOR CVD THIS 7ML, ELECTROPOLISHED, VERTICAL STAINLESS STEEL BUBBLER IS PERFECT FOR LOW VOLUME APPLICATIONS AND IS COMPATIBLE WITH MOST COMMON TOOL TYPES. OUR SMALL BUBBLER WILL MAXIMIZE GAS CONTACT TIME, REDUCE THE AMOUNT OF MATERIAL NEEDED TO RUN TRIALS WHILE PROVIDING THE SAME FUNCTIONS OF A REGULAR BUBBLER.

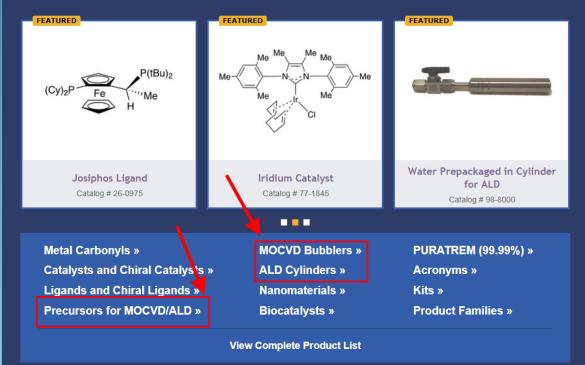




HOW TO LOOK FOR CVD/ALD PRECURSORS & BUBBLERS/CYLINDERS ON THE STREM WEBSITE



We manufacture high quality chemicals and deliver them globally







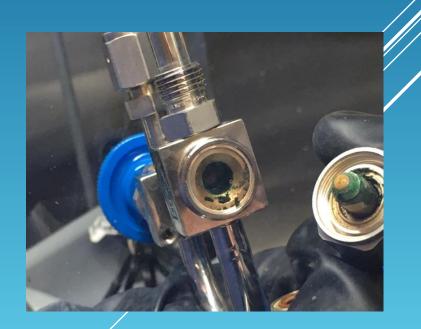
ALD APPLICATION ISSUES: 28-1301

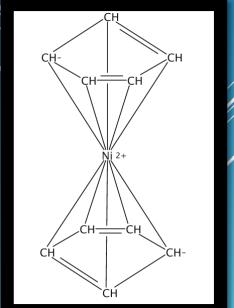
Bis(cyclopentadienyl)nickel, 99% (Nickelocene)

Case study; Blockages reported in ALD Nickelocene cylinders resulting in restricted or lost flow/material delivery









Solids at VCR connection between cylinder and valve

Outlet valve blockage

36



ALD APPLICATION ISSUES

Closer inspection shows decomposition evident



Solids at top of cylinder near valve assembly (viewed via sliced end of cylinder).



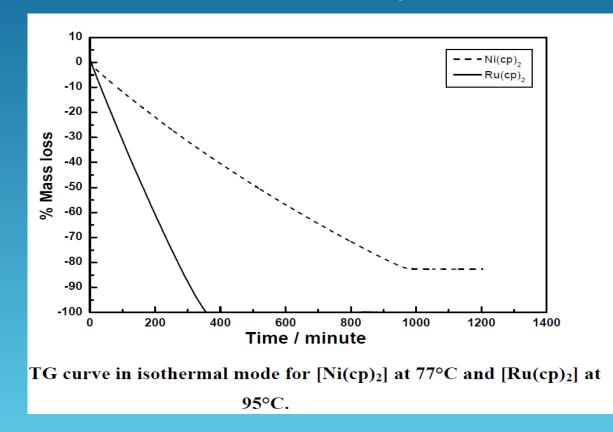
Decomposed (brown) material coating fill port of cylinder.





NiCp₂ is prone to decomposition when subjected to higher temperatures over long timeframes.

Over a short timeframe this decomposition is not detected



Over time (15 hrs at 77 C), the mass loss becomes constant leaving 18% residual mass from decomposition.

38

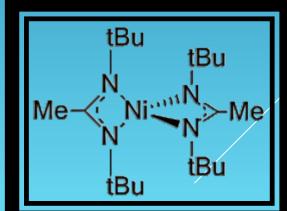
Strem Chemicals

Experimental investigations of thermodynamic properties of organometallic compounds. Thesis; R.A. Siddiqui, section 4.1.3. University of Duisburg-Essen, 2009

Conclusion and Recommendations

- When selecting a precursor for ALD/CVD use, consider carrying out a more prolonged "thermal stress test" as well as the routine shorter term thermal analysis.
- When using Nickelocene, if practical run at lower temperatures (ie. < 70 C) to avoid too much decomposition.
- Similarly, during "non-run time" periods consider decreasing the heat applied
- Where possible consider using an alternative thermally more stable material such as Strem 28-0045.





39

28-0045



THANK YOU!

Corporate HQ Newburyport, MA, USA (48,000 sq feet)



Laboratory Chemicals



High Pressure





-Lab scale to 22 L / 50L glass reactors -ancillary equipment (rotovap, filtration) For larger scale Strem works with partners 1L, 2L & 5, 25

gallon autoclaves