



CMC Associates

December 2017 Meeting

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Outline

- Introductions
- In the news today – Lita Shon-Roy
- TECHCET Analyst Update: Jonas Sundqvist– 20 min
- Joint Session Planning
- Future Meeting Schedules & Wrap up – 1 min.

New News

 www.criticalmaterials.org

 CMC Associates quarterly updates and meeting slides: www.techcet.com

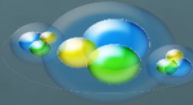


Analyst Introduction

- Jonas Sundqvist, Ph.D. – Sr. Technology Analyst of TECHCET— covers ALD and CVD precursors and related technologies, and is the co-chair of the Critical Materials Council (CMC) Conference. His over 20 years of work experience includes group leader of the High-k devices group at Fraunhofer's Center Nanoelectronic Technologies (CNT), which included 28nm node work for GLOBALFOUNDRIES Fab1. While there, he founded the ALD Lab Dresden together with TU Dresden. At Infineon Memory Development Centre (MDC) he developed high-k and metal nitride ALD processes, and at Qimonda he was a materials manager focused on the ALD / CVD precursors supply-chain. He is the founder of BALD Engineering, an independent blog and networking platform for ALD. He holds a Ph.D. and a M.S. in inorganic chemistry from Uppsala University, Sweden, a B.S. in electrical and electronics engineering from Lars Kagg, and nine patents.



Electronics Materials Information



Dielectric, Metal & High-k Precursors

December 11, 2017

By Jonas Sundqvist, Ph.D., Sr. Analyst

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Readers' Note:

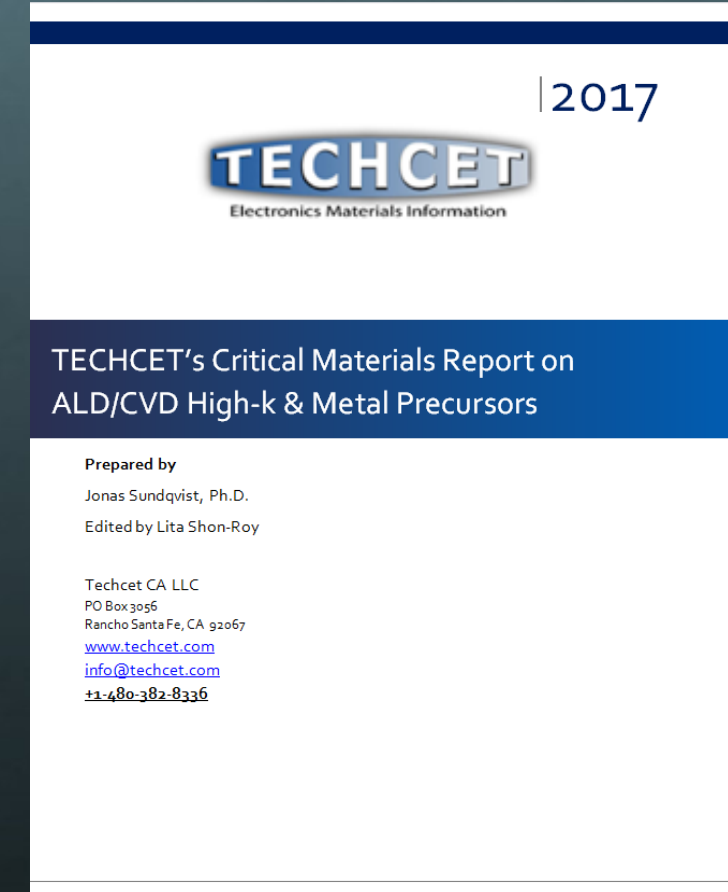
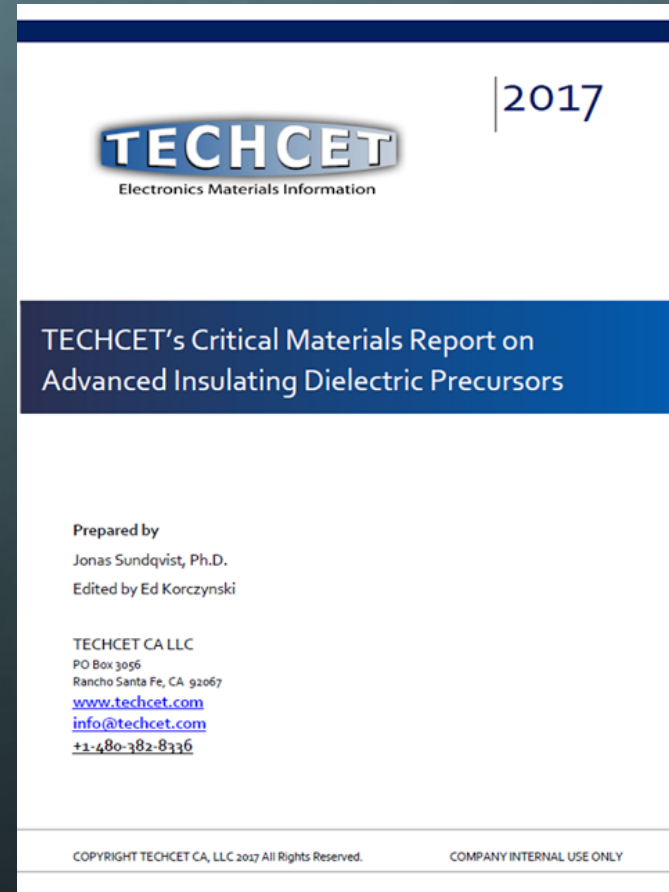
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Precursors

- TEHCET Cover Dielectric Precursors and ALD/CVD Metal and High-k Precursors in two Critical Material Reports
- Customized Combination Reports can also be compiled



Outline

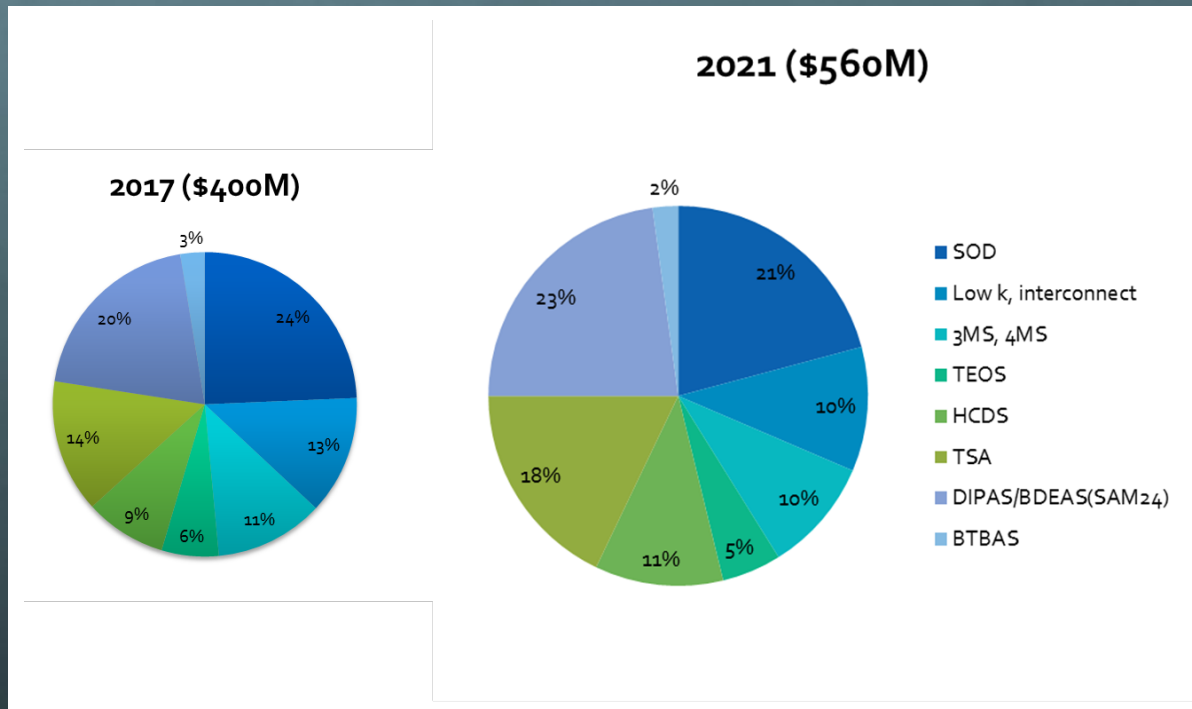
- 🌐 Company Profiles, Mergers and Acquisitions
- 🌐 Forecast for solid metal ALD & CVD precursors
- 🌐 Metal sourcing, supply chain and pricing (e.g. Co, Zr, Ru)
- 🌐 New applications (e.g. MOx Hardmask, SiO₂ ALD layers)
- 🌐 Precursor Delivery Systems
- 🌐 Emerging markets (e.g. PV, OLED, Li-Batteries, Cemented Carbides)
- 🌐 ALD & CVD OEMs

Precursor Growth drivers

To summarize, the wafer production yielding growth in dielectrics and metal precursors for deposition over the next 3 to 4 years will be driven by:

- 🌐 Multiple patterning using Self-Aligned Double Patterning and Self-Aligned Quadruple Patterning (SADP & SAQP) for leading edge technologies,
- 🌐 Advanced logic as 10nm followed by 7nm moves from qualification into production,
- 🌐 2D-NAND to 3D-NAND transition,
- 🌐 DRAM recovery, scaling may be back after Samsung announce 10 nm DRAM w/ EUV
- 🌐 China investments in new fabs and supply-chain expansions, and
- 🌐 IoT and automotive applications driving demand for legacy nodes.

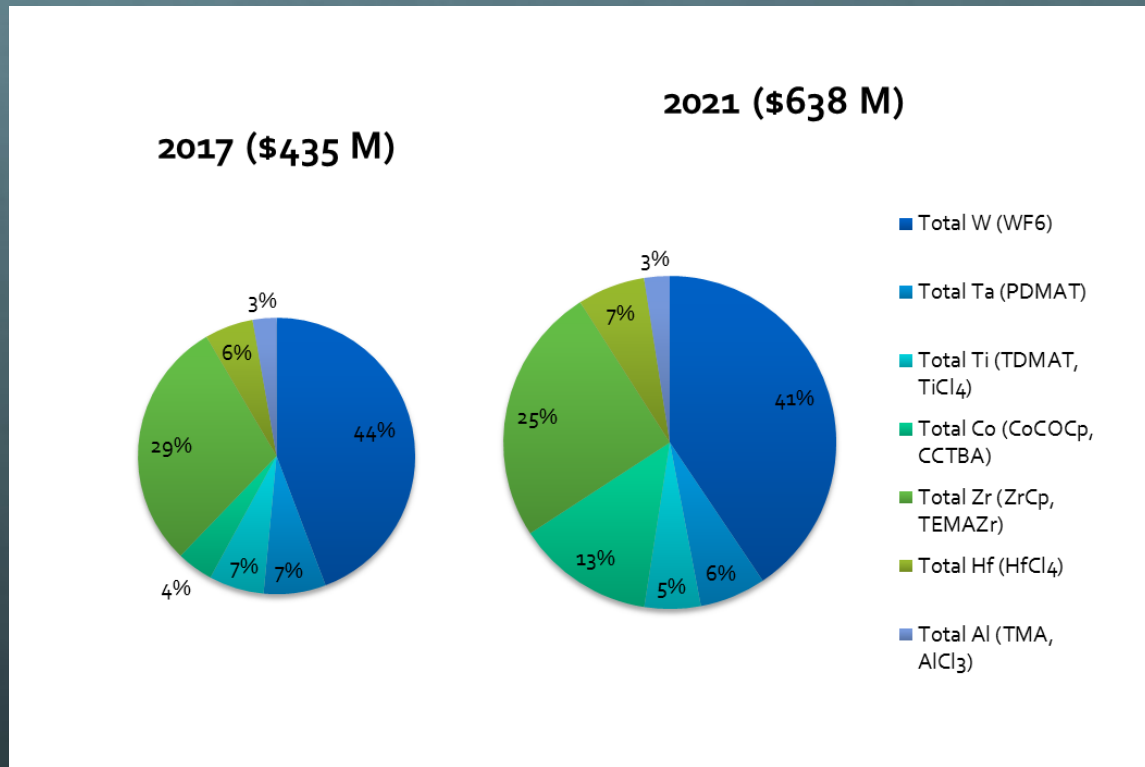
Dielectrics precursors



The total market for 2017 is estimated to US\$400M, growing to US\$560M in 2021. Current growth over 10% is expected to slow slightly to be in the 8-10% range over 2019-2021. Anticipated near-term developments include transitions from CVD to ALD for several IC fab modules.

Besides the Low-k and Spin on Dielectric precursors, CVD and ALD dielectric precursor market segmentation be made according to materials and applications: BTBAS, DIPAS, BDEAS, 3DMAS, 4MS, 3MS, TEOS, TSA and HCDS




Metal & High-k Precursors



The combined markets for ALD and CVD metal precursors are estimated to reach approximately to US\$435M 2017 and above US\$638 by 2021.

The market has had a double digit growth over an extended period of time. We expect the market to continue to develop healthy as the transition to 10nm- and 7nm-node logic and 3D-NAND take place, with an average long term CAGR of 11% over 2013 to 2021 and the possibility of acceleration further to 14 to 16% toward 2020/2021.

Company Profiles, Mergers and Acquisitions

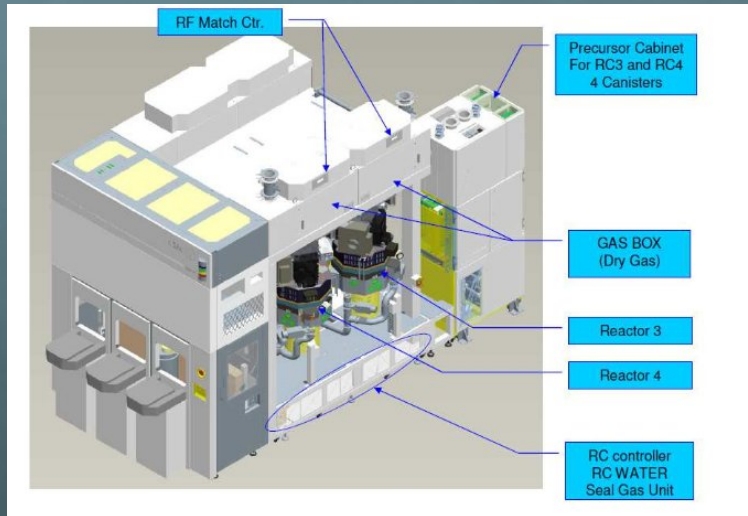
-  Techcet is tracking the big players as well as the smaller suppliers and sub-suppliers
-  up to 30 companies and growing)
-  Face to face briefings and conference calls

Adeka.....
Air Liquide S.A.....
Azmax part of Azuma group
BASF.....
DNF "Dream New Future"
Dow Corning
Digital Speciality Chemicals (DSC).....
Dow
Entegris (previously ATMI).....
Epivalence.....
Fujifilm.....
Gelest, Inc.....
H.C. Starck.....
Kojundo Chemical Laboratory
Merck's EMD Performance Materials (previously Epichem, SAFC Hitech and AZ).....
Nanmat Technology Co. Ltd.....
Norquay Technology.....
Nova-Kem LLC.....
Nanogen Solutions
Pegasus.....
Praxair
Soulbrain Co., Ltd.....
STREM.....
TCI Chemicals.....
Tri Chemical Laboratories.....
Umicore
UP Chemical Co., Ltd.
Versum Materials, Inc. (previously Air Products Chemical Inc.).....

Liquid Precursor Delivery Systems

- DRAM fabs, that traditionally use more LPCVD and ALD furnace equipment, pioneered the introduction of Liquid Precursor Delivery Systems (PDS) technologies for standard precursors and novel low vapor pressure metal organic precursors such as hafnium and zirconium.
- This has led to the replacement of traditional on-board source delivery by either direct liquid injection or auto refill units connected to the on-board sources (see next slide)
- For new fabs most liquid precursors will be supplied by auto refill, liquid precursor delivery systems (4 to 40 L) and in many cases also bulk fill (>100 L)
- TEHCET has started to track the PDS market for liquid and solid precursors. Please contact TEHCET for more details.

Liquid Delivery Systems → Bulk fill



PECVD Tool with fab floor PDS cabinet (e.g. ASM Eagle Dielectric CVD, fabsurplus.com)

Fab level

Process chamber / tube precursor evaporation supplied by

- A. Onboard supply
- B. Onboard + Auto refill
- C. Precursor Delivery System

Processing Equipment



PDS



Valve Manifold box

Sub Fab level / Service Area

Precursor Evaporation supplied by

- A. Precursor Delivery System / Auto refill
- B. Bulk Delivery System

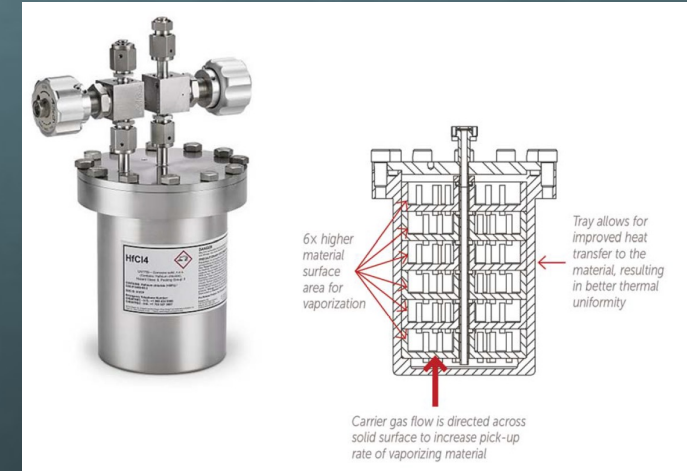
Liquid precursor supply system designed to interface directly to OEM process tools. (Modified from Versum Materials promotional material 2017).

Forecast for solid metal ALD & CVD precursors

Solid precursors are still predominantly delivered by on board sources and examples of those include:

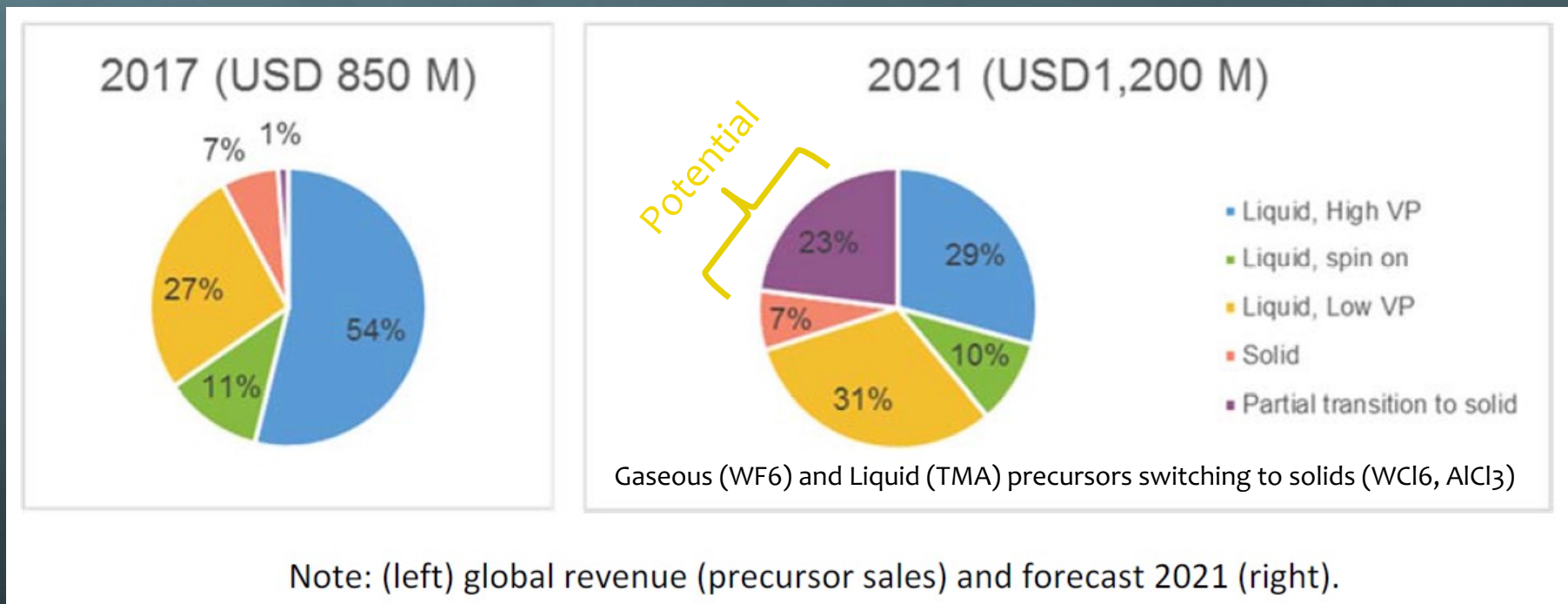
- HfCl₄ and La(TMDH)₃ (Logic Gate stack)
- PDMAT (TaN Cu barrier)
- Solid metal halides (AlCl₃, WCl₆, TaCl₅ and TaF₅).

Entegris has shown larger volume delivery systems for Tungsten (WCl₆) and Aluminium (AlCl₃) in 3D-NAND manufacturing (right)



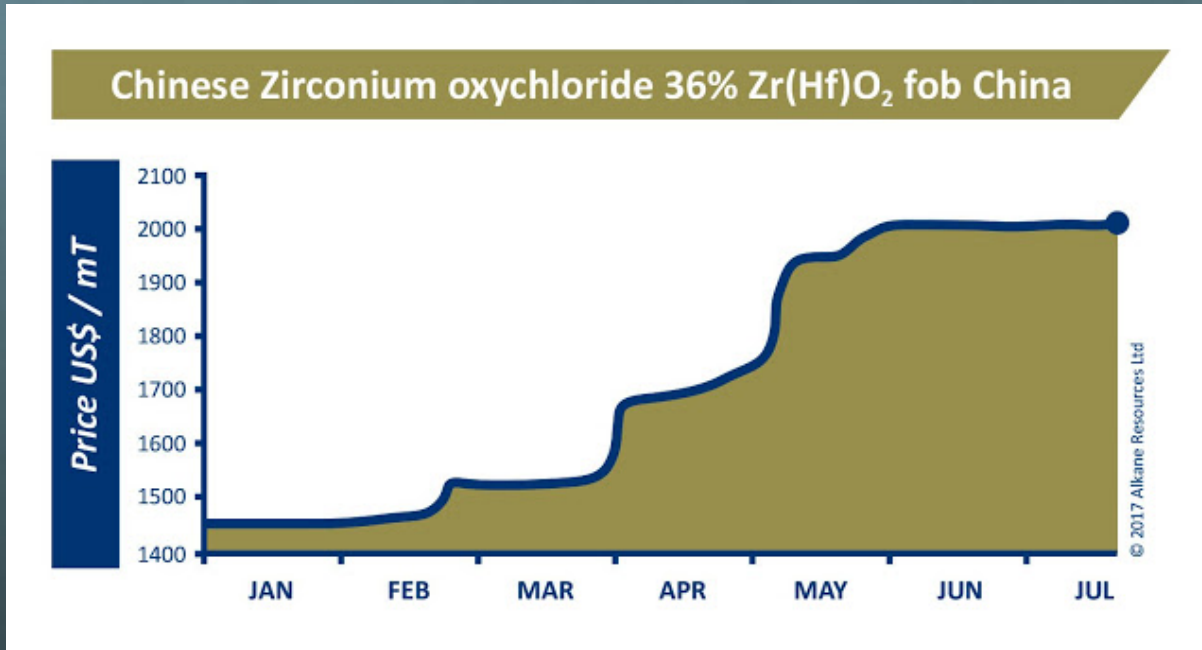
Updated forecast for solid precursors

As bulk delivery technology of solid precursors improve - The total servable market for solid precursors could grow 20 to 30% next 5 years (~10% per year).



The total SoD, ALD and CVD precursor market 2017 (Dielectric, Metal and High-k) is about US\$ 850 M and is forecasted by TECHCET to be US\$ 1,200 M in 2021 (see report for detailed segmentation)

Zirconium oxychloride (ZOC) prices are up 40% since January 2017



For the semiconductor industry, Zr is commonly used in hi K precursors (DRAM capacitors)

Alkane Resources reports that zirconium oxychloride (ZOC) prices up 40% since January 2017, which are the highest prices for 4-5 years.

Zr is commonly used for the metal components of nuclear reactors – especially the claddings of their nuclear fuel rods. This property makes it **crucial to the expanding Chinese nuclear** industry and is one of the main reasons for the current upward price trend.

Zirconium is mainly used for the ZrCp precursors and ALD deposited ZrO₂ in DRAM memory cell capacitors. ZOC is also the main source for the >50 tons global demand of hafnium of which about 2 tons is heading for the electronics and semiconductor industry – mainly Hafnium chloride (HfCl₄) for the Logic Gate Stack (HKMG). **TECHCET estimates ~10% to 20% of the Zr precursor price is from Zr metal costs; until recently, this cost of the metal had been relatively small.**

Cobalt pricing

5 YEAR



1 YEAR

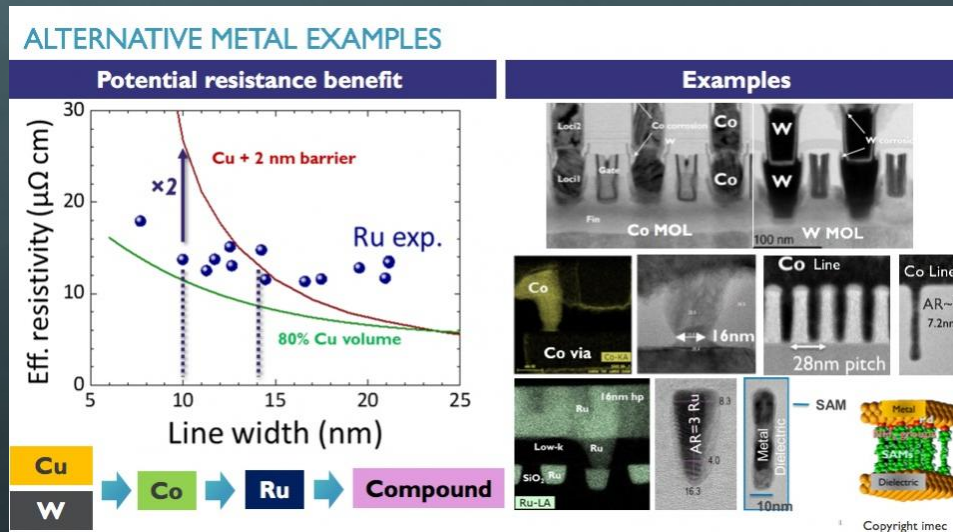


- Cobalt is used for cemented carbides and lithium battery
- Cobalt is seeing more usage in IC interconnection applications. Due to this we are following the Cobalt market in terms of supply and demand.
- Semiconductor usage is only < 1% of global demand.
- The key concern is that after several years of an oversupplied market and weak cobalt prices, the market in 2017 is very dynamic with Metal Bulletin's High Grade Free Market price increasing from US\$15/lb at the start of the year to over US\$28/lb in September.

Cobalt to Ruthenium to Manganese - development for interconnects

Cobalt is one of the materials that offers benefits of lower resistance or improved electromigration for BEOL interconnects. We are seeing active development and adoption of cobalt for certain layers, and electroplating of cobalt may be a cost-effective solution rather than ALD/CVD deposition.

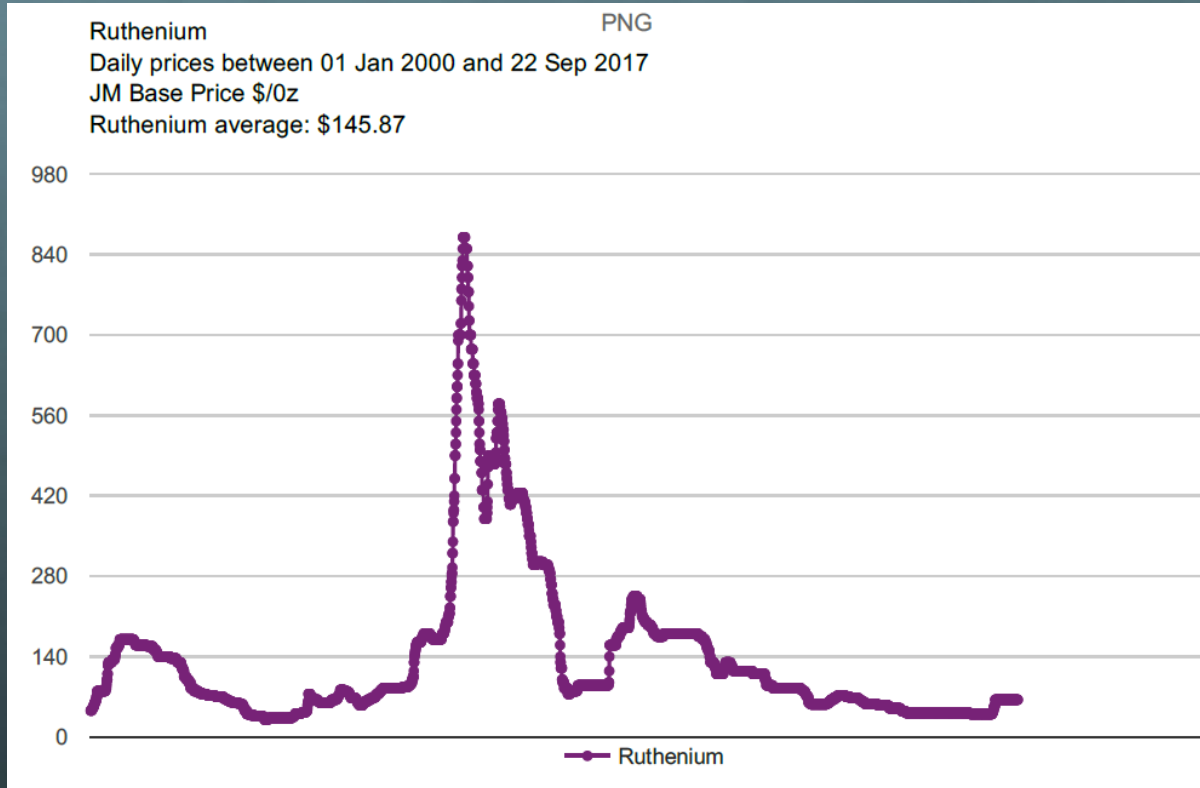
Other candidates, such as **ruthenium** for the liner and **manganese** for the barrier, are in R&D at Imec and Leading IDM/Foundry Industry that are exploring other materials for the BEOL.



Imec has had a Ruthenium program since 2009, originally aimed at DRAM but later moved to focus more on future interconnects.

The Effective resistivity as a function of linewidth for copper and ruthenium (left) and metallization examples for copper, tungsten, cobalt and ruthenium (right). Image courtesy of IMEC, SEMICON WEST 2017, Zsolt Tokei presented "How to Solve the BEOL RC Dilemma".

Ruthenium Pricing



TEHCET estimates 40% of Ru precursor cost is from the Ru metal price.

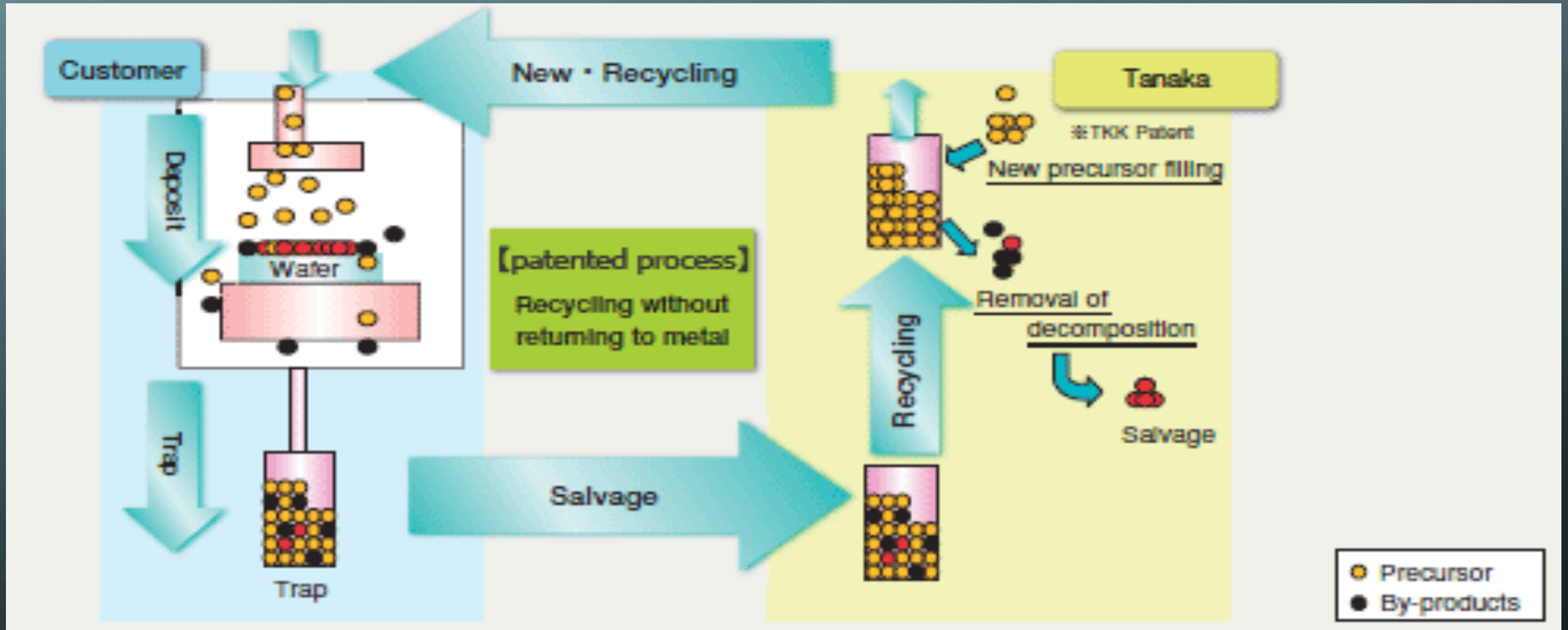
Ruthenium had a very volatile pricing 2000 to 2010 due partially to two reasons:

- use of Ruthenium in magnetic hard disk drive industry
- potential implementation for DRAM

Since then the magnetic hard drives are being replaced by SSDs and the ruthenium introduction for DRAM never came and pricing has been stable for 5 years.

Ruthenium pricing, Johnson Matthey 2000 to 2017

Ruthenium Recycling Available Technology



Ref:TANAKA

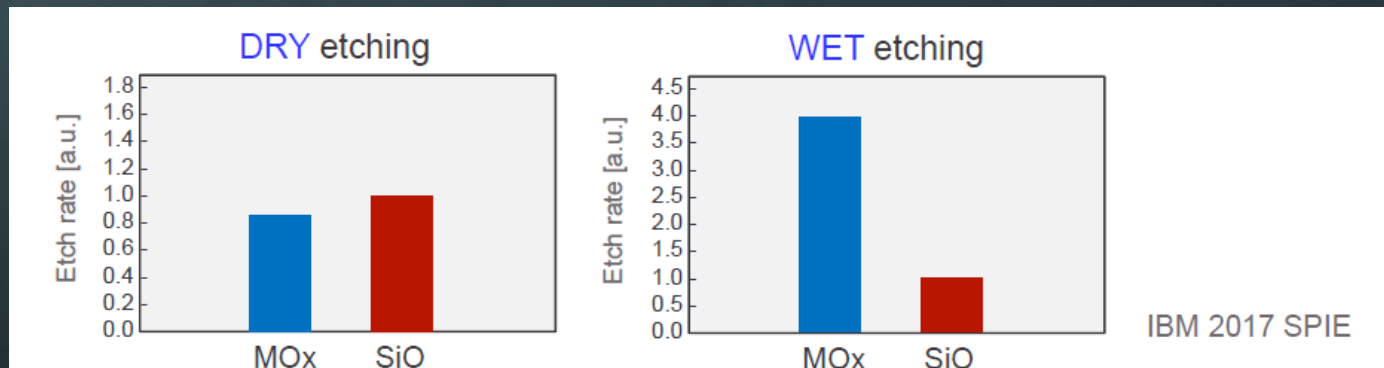
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IBM and ASM ALD Show Etch Selectivity using M-oxide hardmask for multipatterning processes

Process	Thickness	Precursor	Passes
Gate Dielectric - Logic HfO ₂	2 nm	HfCl ₄	1 X
Capacitor - DRAM ZrO ₂	6 nm	ZrCp	1 X
Multi- patterning MOx Hardmask - 3D NAND and Logic	3 nm	Not known	> > 1 X

Currently, most metal precursors were used for capacitor and gate dielectric materials. i.e. Precursors for Al₂O₃, ZrO₂ and HfO₂.

However, new development shows improved etch selectivity for metal-oxide hard mask materials used for multi-patterning, as shown below. If implemented the process has the potential of greatly increasing the volume demand of these MO precursors.

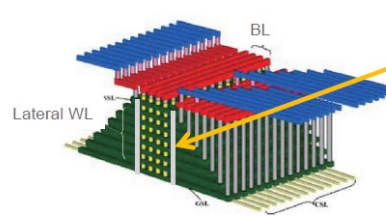


ASM PEALD SiO₂ for 3D-NAND

Applications for ALD SiO₂ precursors continue growing starting from 3D NAND applications and sub20nm DRAM...

ALD FOR 3D-NAND APPLICATIONS

ASM



(1) Source contact/separation slit

SiO

Poly-Si or W

Samsung VLSI Symp 2009

(1-1) High quality PEALD SiO for slit sidewall protection of source contact

Low temperature & high quality SiO without damaging WL metal

WL

(1-2) High quality PEALD SiO for slit fill

- High quality conformal SiO
- Low temperature process is needed for top select gate separation after WL fill

TechInsights

ALD FOR SUB-20NM DRAM

ASM

1. Bi-directional SDDP for hole patterning, introduced in D1x (LT-PEALD SiO)

Storage Node Contact

BL

bWL

W

BL

2nd SDDP

Filling

PMD SiO after 1st SDDP

2 times SDDP

Top view (TechInsights)

Cross sectional view (TechInsights)

2. Sacrificial SiO (LT-PEALD SiO)

TiN bottom electrode

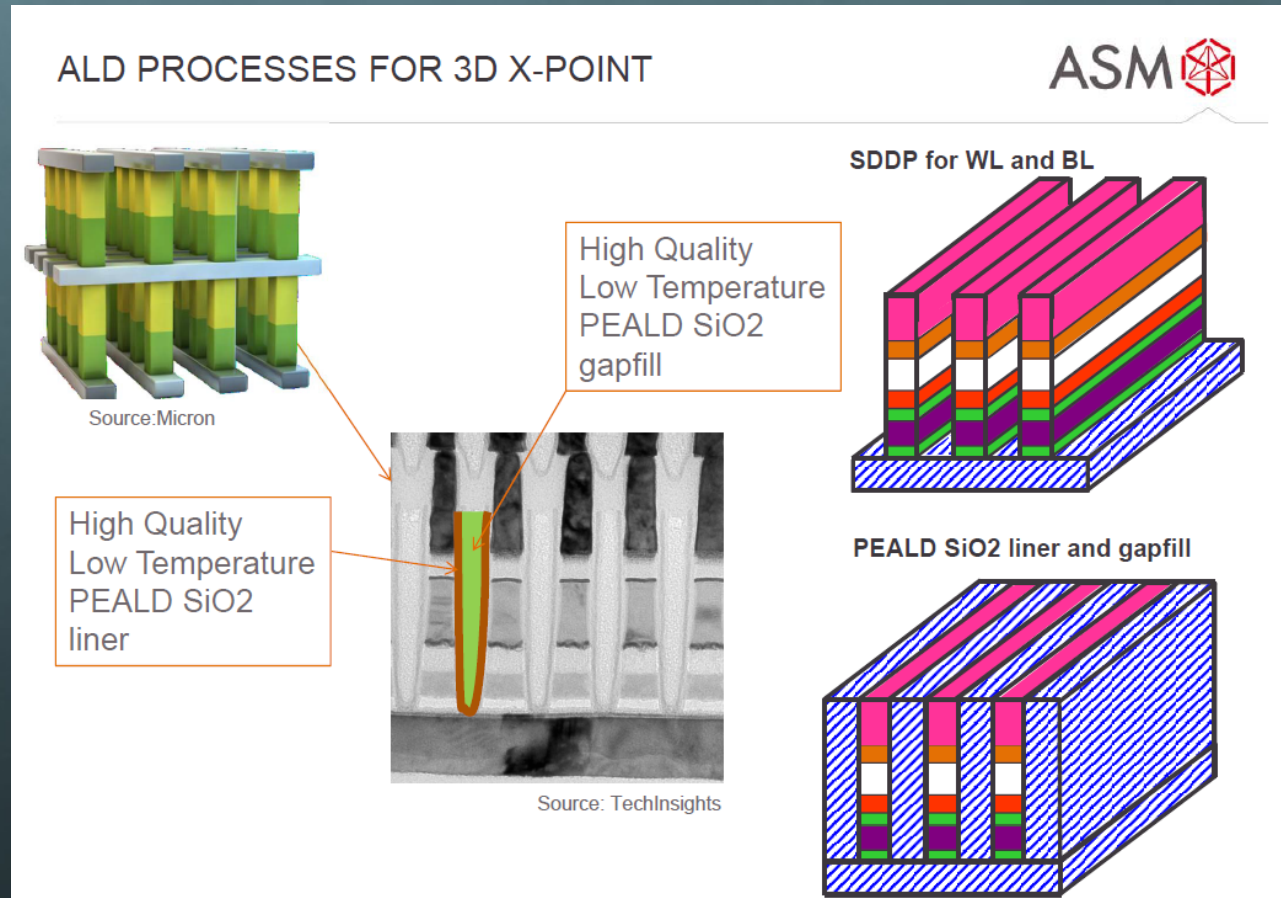
SiO sacrificial fill

Slit formation → SiO removal

Dielectric / metal deposition

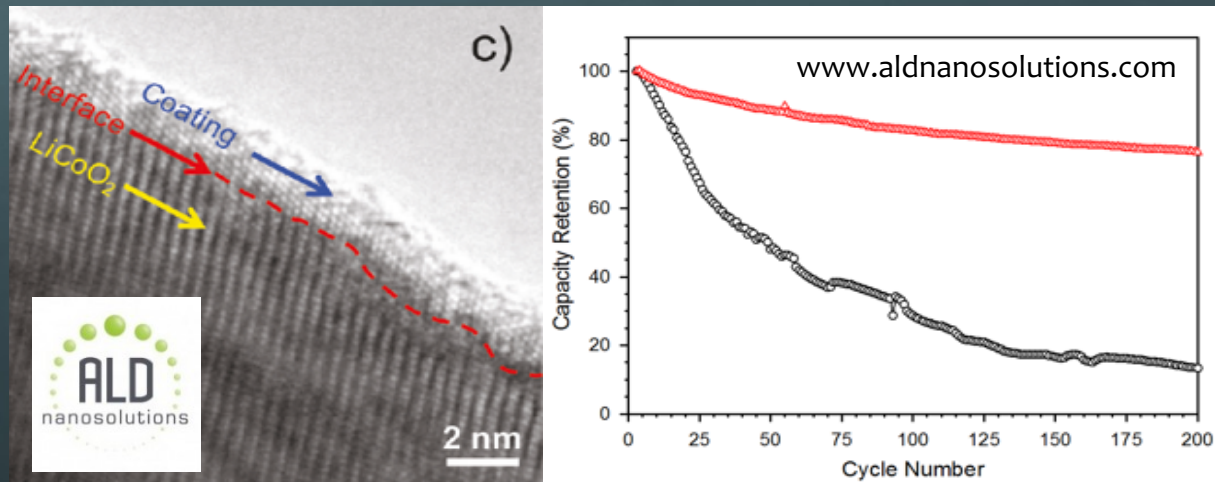
ASM PEALD SiO₂ liner and gap fill for 3D X-point

... to 3D Xpoint and advanced memory devices.



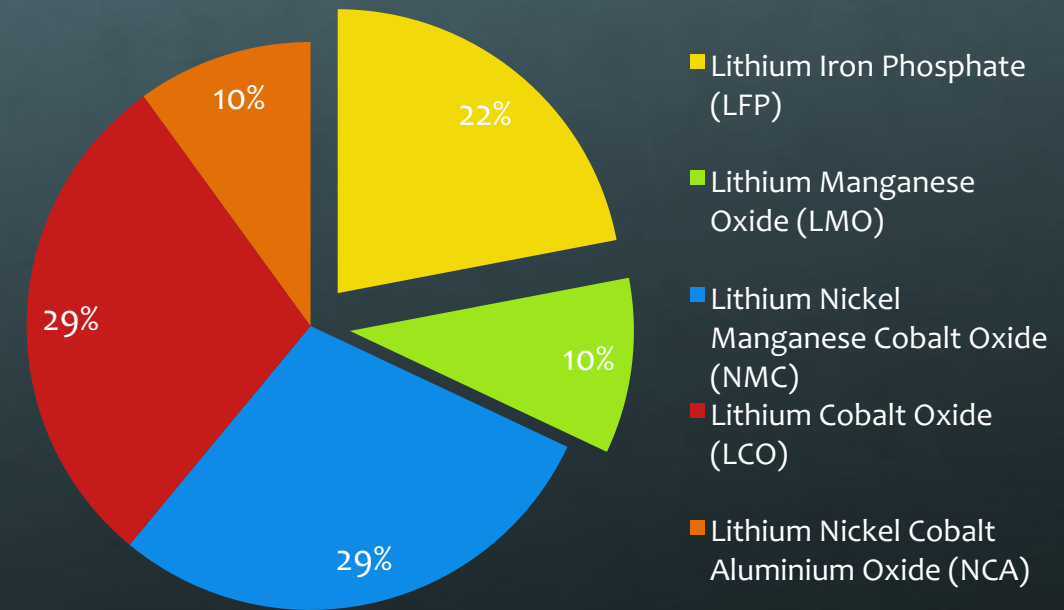
Lithium batteries – competing market for Ni, Co, Mn and ALD Precursors (ALD in development)

- Competition for Cobalt (See Umicore presentation)
- New Powder ALD Technologies for barriers are in Pilot Production



ALD NanoSolutions we have completed modeling that indicates scaled up cost on the order of \$1/kg to production. Currently offering batch or fully continuous scale up solutions

Break down of Lithium batteries by type



(Research in China 2015)

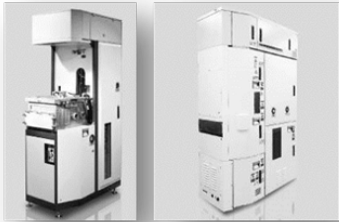
ALD & CVD OEMs Market-

a general indicator of where the precursors are being sold

Precursors, Hardware & Technologies

2016 ALD Equipment market
USD 1.3 Billion

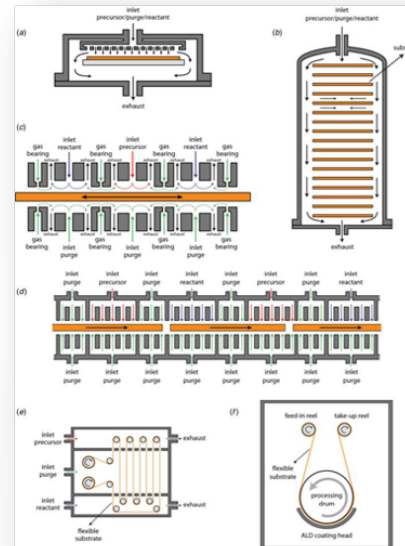
Single Wafer



Multi Wafer



Reactor Types

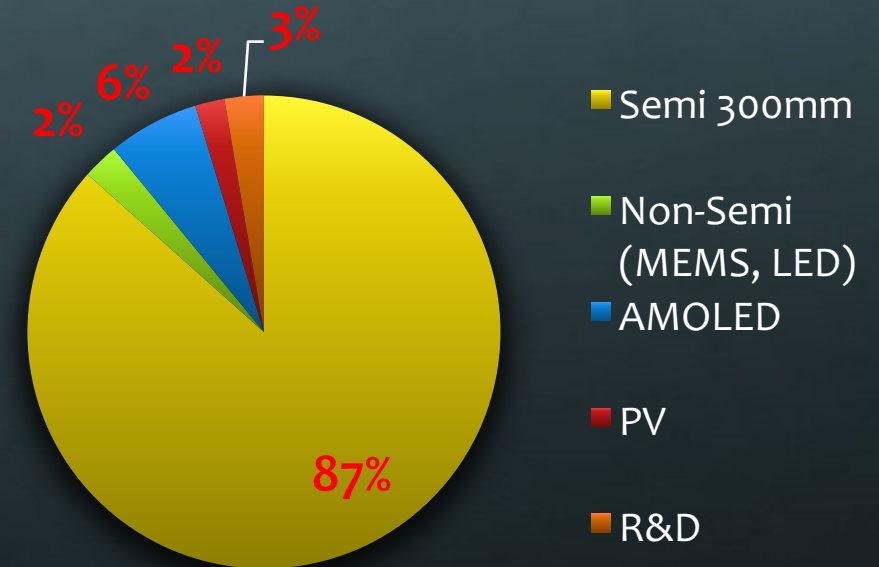


J A van Delft et al 2012 Semicond. Sci. Technol. 27 074002

Large Batch



Spatial ALD



Summary

- Expected continued growth in Si-dielectric precursors for Logic & Memory Patterning (SADP, SAQP) and 3DNAND (dielectric stack)
- High-k precursor market segment is dominated by Zr for DRAM and Hf for HKMG
 - many applications using Hf on the horizon (FRAM, RRAM)
- ALD / CVD metal precursors volume is dominated by W, Ta and Co is starting to grow now
- Competing industries in HVM (MEMS, PV, AMOLED) are mainly consuming Al (TMA)
- ALD / CVD Quarterly update next month will include info on China suppliers as well as updated forecast

Thank you!

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ww.cmcfabs.org

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Joint Sessions

Purpose of Joint Session:

to problem solve and/or create better understanding for future collaborations

Please contact Diane if you are interested in being part of the task force who will organize the
Joint Session Scheduled for April 25, afternoon. Dscott@Techcet.com

- Topic of interest: PCN (process change notification)
- Problems:
 - PCN notification period may be prohibitively long limiting the degree to which a supplier may be able to cost reduce via changes in parts or process. In the meantime, constant price pressure is being applied.
 - PCN terms and definitions are not always clear up front causing confusion, cost and loss of time.
 - Automotive industry is requiring up to 10 years PCN notification, this is highly unreasonable but there appears to be no organized remedy to this mismatch in industry requirements. 1 year change notification in Semi is not uncommon.

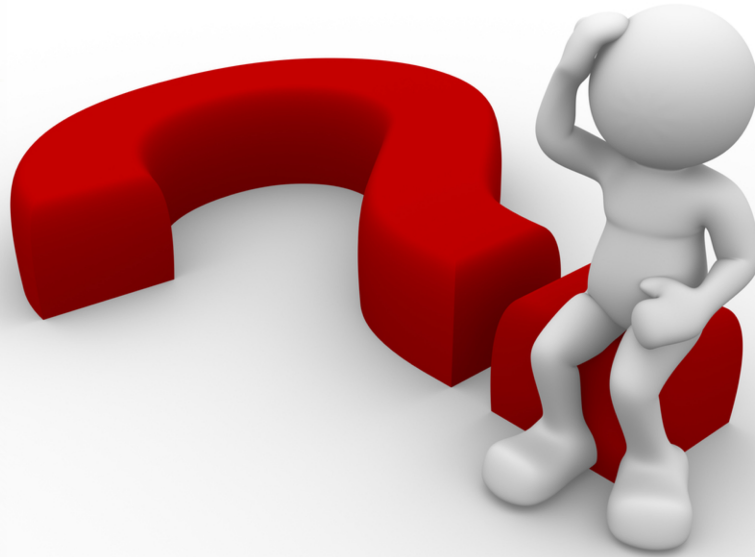
Working template for discussion:

- Defining key terms
 - What terms are used to tell the supplier / maker that a PCN (process change notification) is required
 - Process change – what does this mean? Categorize
 - ———
- What are the costs associated with these pcn notifications
- PCNs are often done for the purpose of cost reduction – but can't do it if it's not permitted, yet end users require costs to decline every year.
- What is the term (time period required)

Future Meetings / CMC Conference 2018

- ❑ CMC Monthly – January 24 – Silicon Wafers
- ❑ CMC Joint Session - Fabs & Supplier members – April 25, 12:30 pm – 4pm
- ❑ CMC 2018 F2F and Conference– **April 24-25 and April 26-27** respectively Phoenix, AZ (Chandler area)
 - ❑ Working on host confirmation now and hope to get confirmation soon
 - ❑ Conference will focus on a blend of business and technology interests
 - ❑ Call for papers has went out – looking for presentations which deal with future materials and practical supply chain concerns addressing the semiconductor industry
- ❑ Please contact edk@Techcet.com for additional conference information

Discussion



Happy Holidays and a Fruitful New Year!

