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Use of plasmas in atomic layer deposition processes

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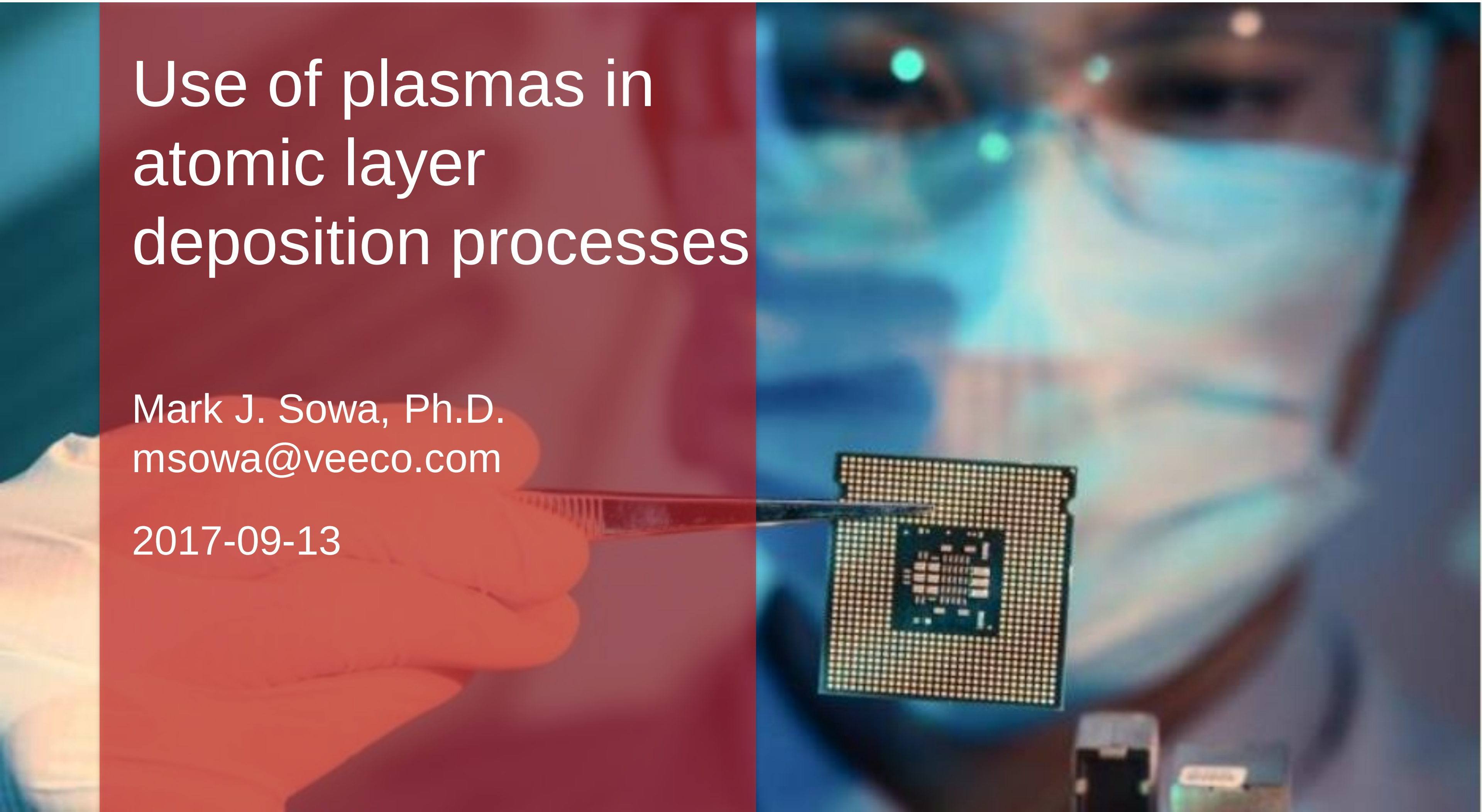


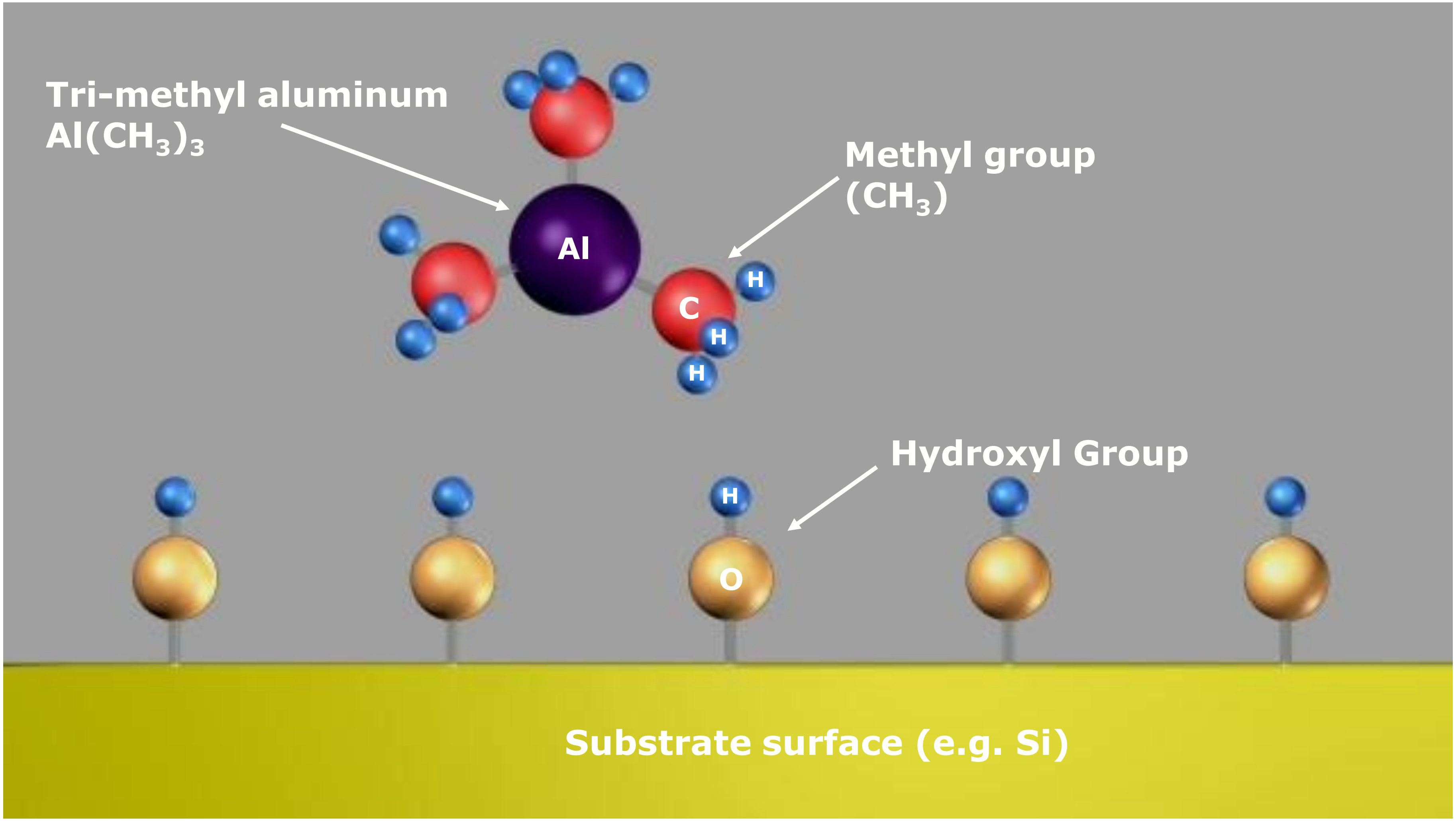
Outline

- Atomic Layer Deposition (ALD)
- Plasma-Enhanced ALD (PEALD)
- PEALD vs ALD
- PEALD Gases
- PEALD Materials
- PEALD Hardware
- Plasma vs Thermal ALD Results
- Our Recent PEALD Results
- Substrate Biasing
- Other Plasma Uses in ALD
- Final Comments

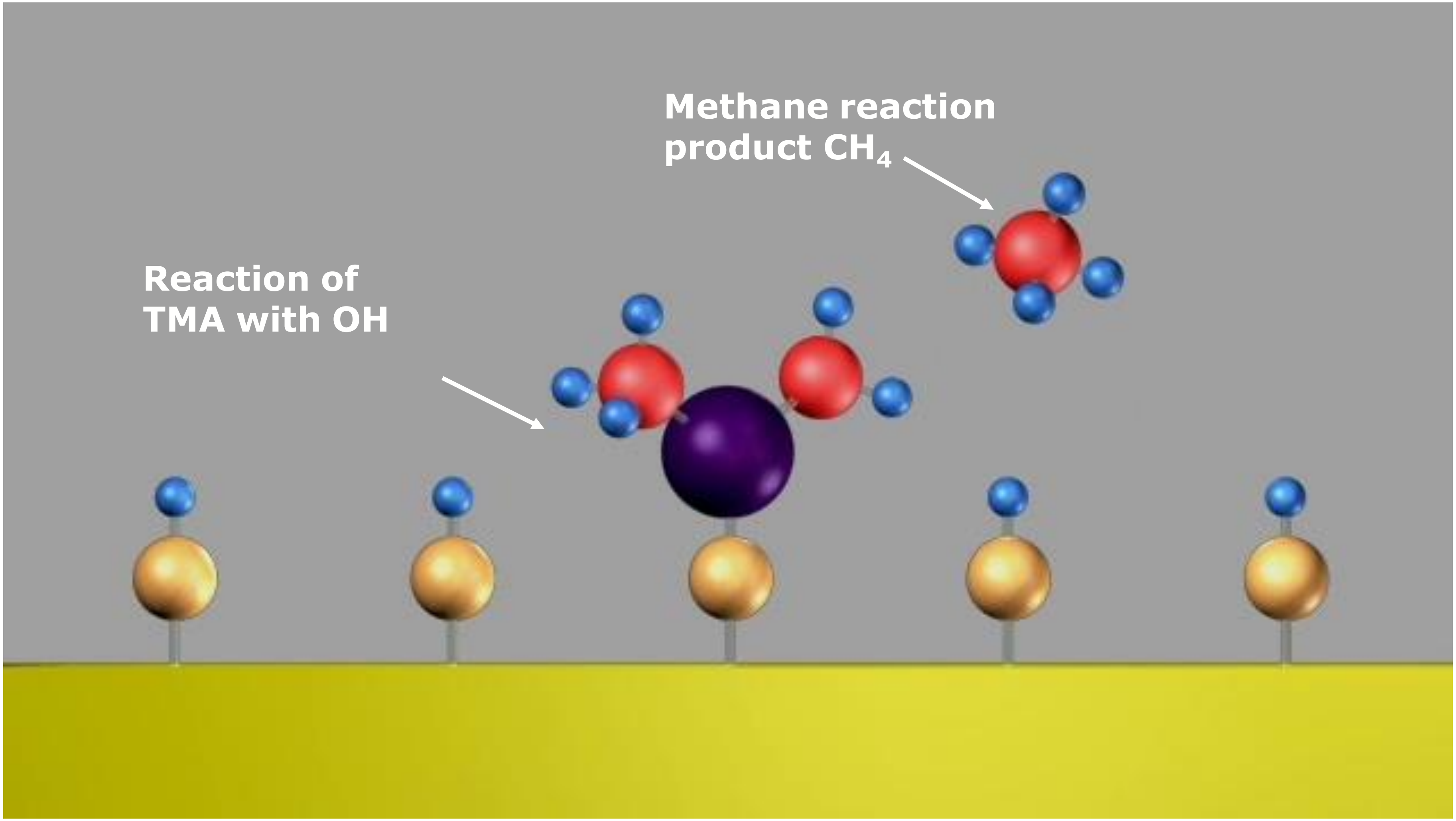
Atomic Layer Deposition 101

- Cyclic thin film deposition technique
  - Substrate exposed to a first precursor containing an element desired in the final film. Precursor chemically reacts with existing surface groups on substrate.
  - Excess, non-chemisorbed precursor is pumped away.
  - A co-reactant is introduced, chemically reacting with the chemisorbed precursor, generating a sub-monolayer of the desired material, preparing the surface for next precursor cycle.
  - Excess, non-chemisorbed co-reactant is pumped away.
  - Repeat until desired film thickness is achieved.

Al_2O_3 ALD Step 1 – TMA Pulse



Al_2O_3 ALD Step 1 – TMA Chemisorption



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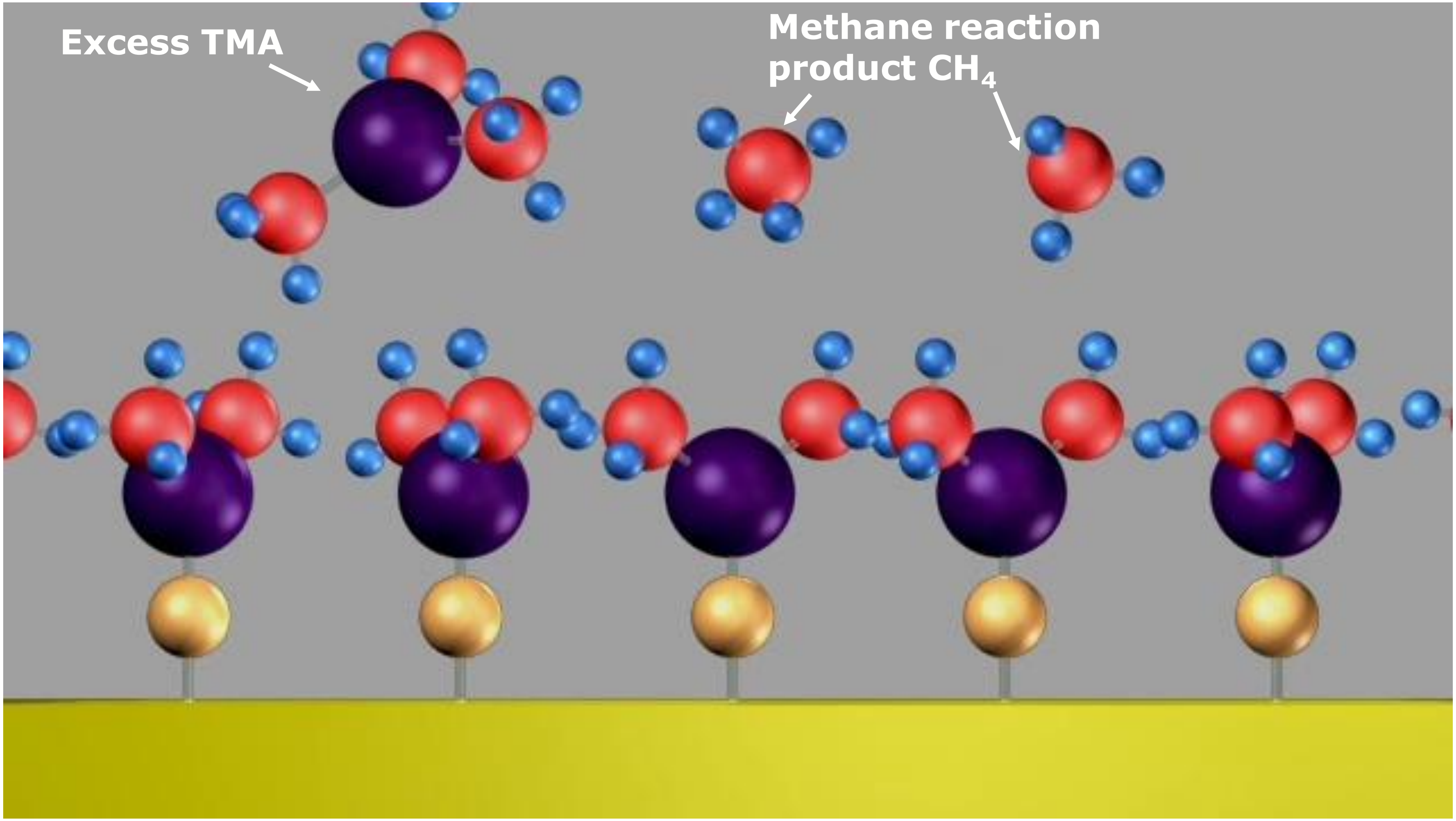
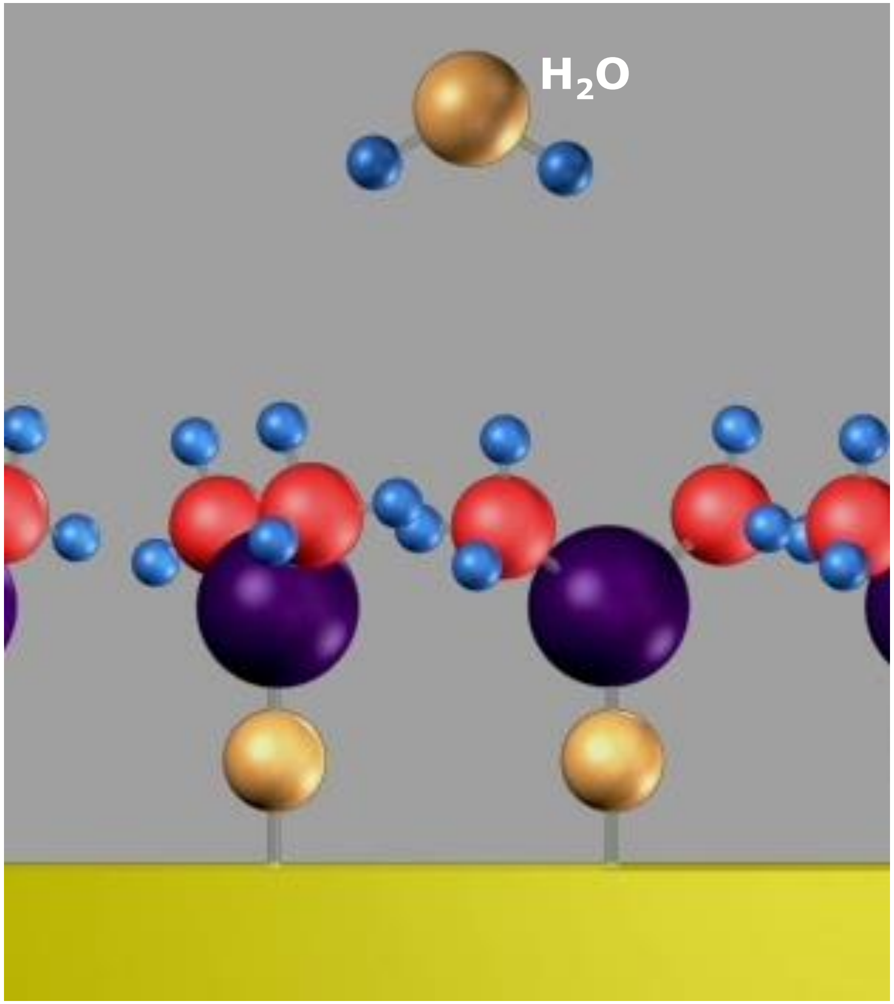
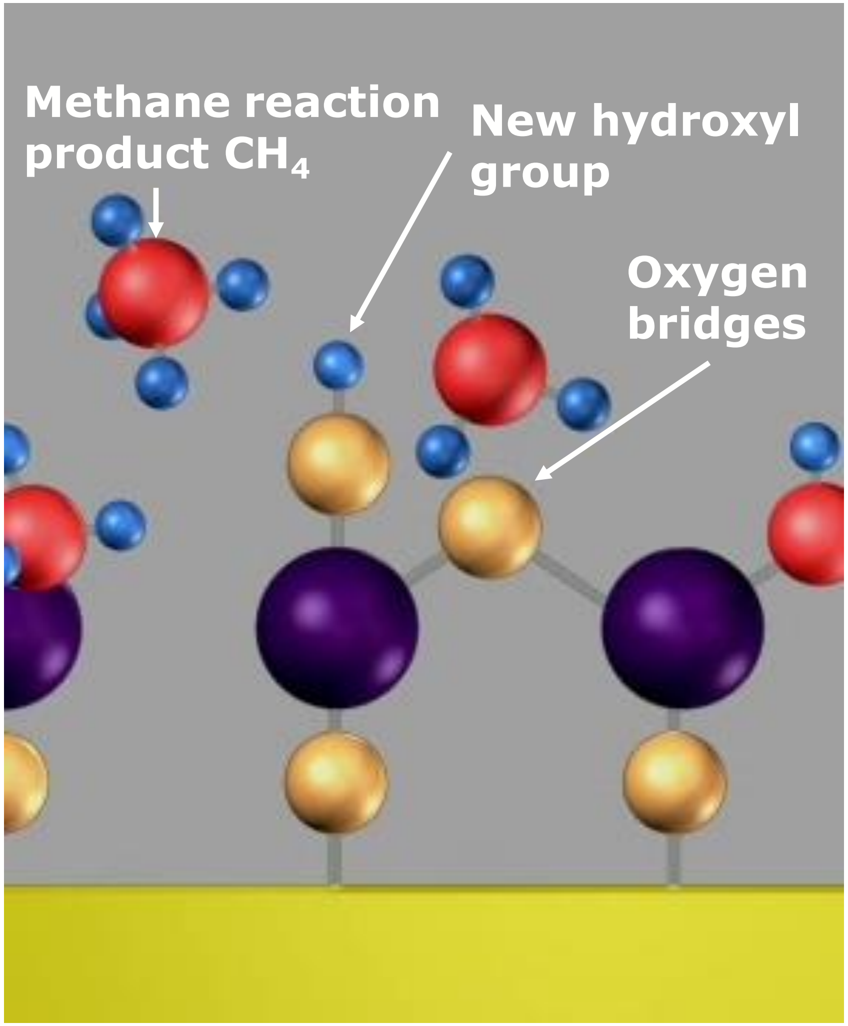
Al_2O_3 ALD Step 2 – TMA Purge



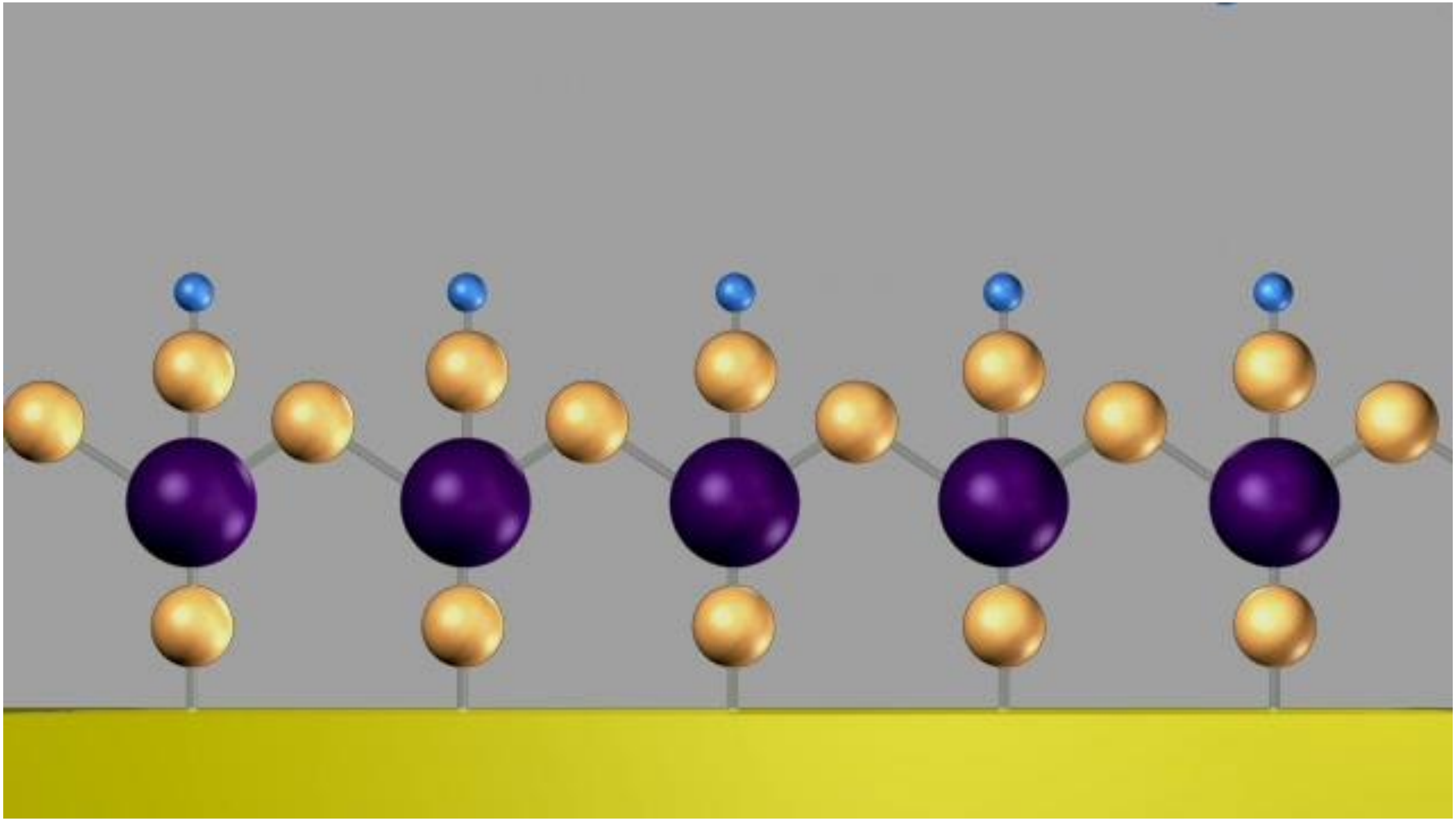
Al_2O_3 ALD Step 3 – Oxidation



Al_2O_3 ALD Step 3 – Oxidation



Al_2O_3 ALD Step 4 – Oxidant Purge



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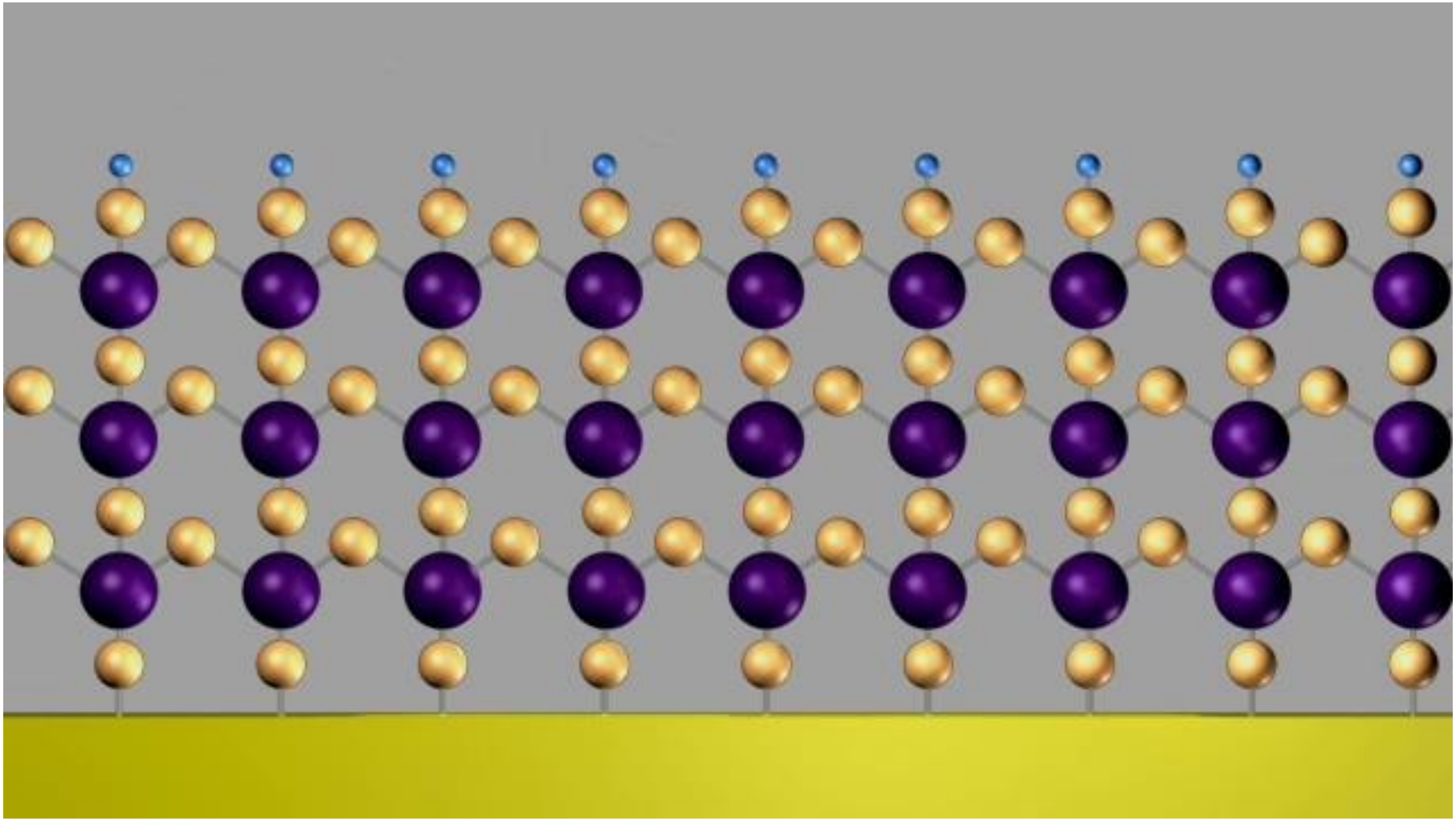
Repeat



ALD Benefits

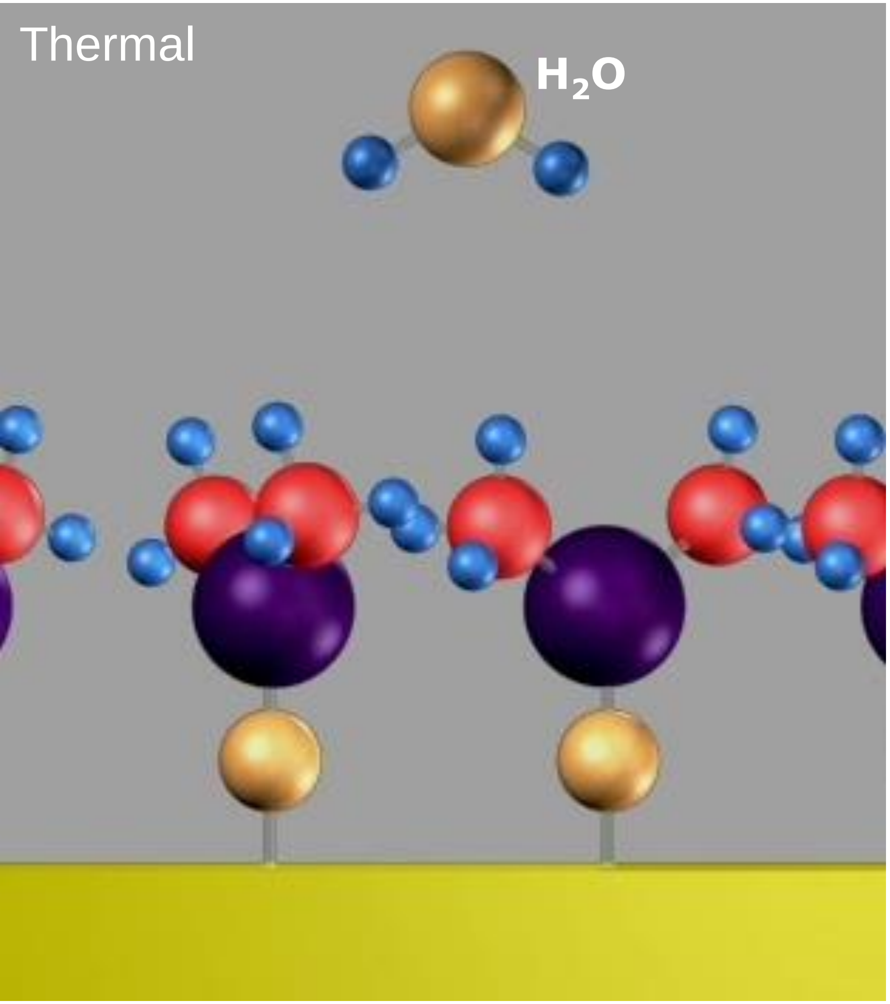
- Wide range of available materials
- Ability to mix different film chemistries to gain the advantages of doping and laminating
- Angstrom level film thickness control
- Excellent uniformity over large substrates
- High aspect ratio conformality
- Good film adhesion
- Moderate deposition temperatures and vacuum levels require relatively simple hardware

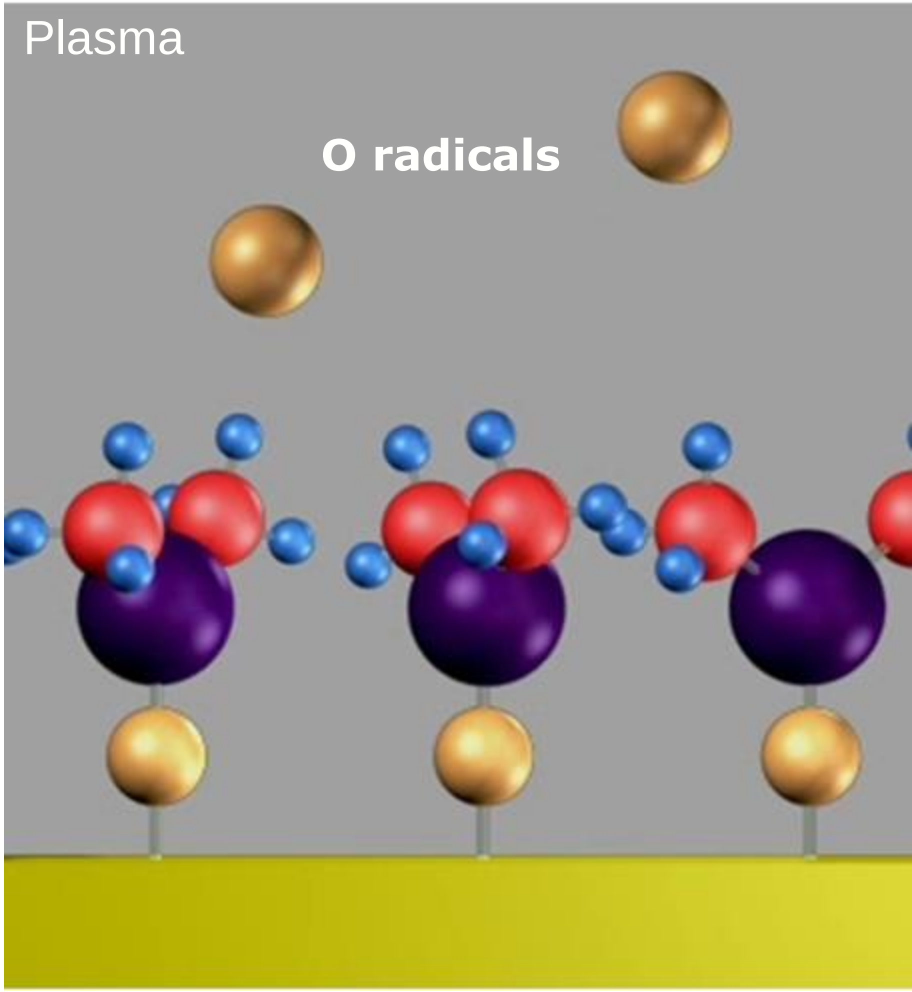
Plasma Enhanced ALD

- Co-reactant is replaced by plasma generated species
- In our Al_2O_3 example, the H_2O pulse step is replaced with an O_2 plasma step
- A combustion-like process occurs between the O-radicals and the methyl groups of the chemisorbed TMA[1]
- In situ FTIR studies indicate O_2 plasma step results in a hydroxyl terminated surface[2]

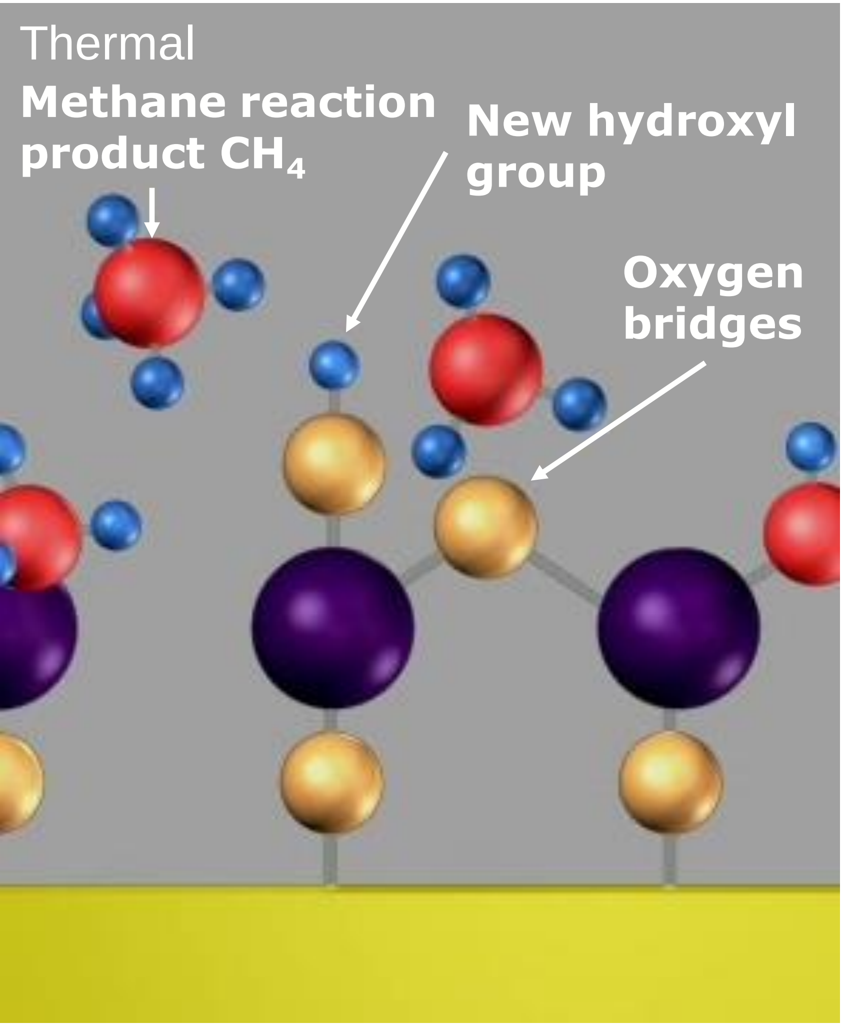
1. S.B.S. Heil et al., “In situ reaction mechanism studies of plasma-assisted atomic layer deposition of Al_2O_3” Appl Phys Lett 89, 131505 (2006)
2. V.R. Rai, et al., “Surface Reaction Mechanisms during Ozone and Oxygen Plasma Assisted Atomic Layer Deposition of Aluminum Oxide” Langmuir, 2010, 26 (17), pp 13732-13735.

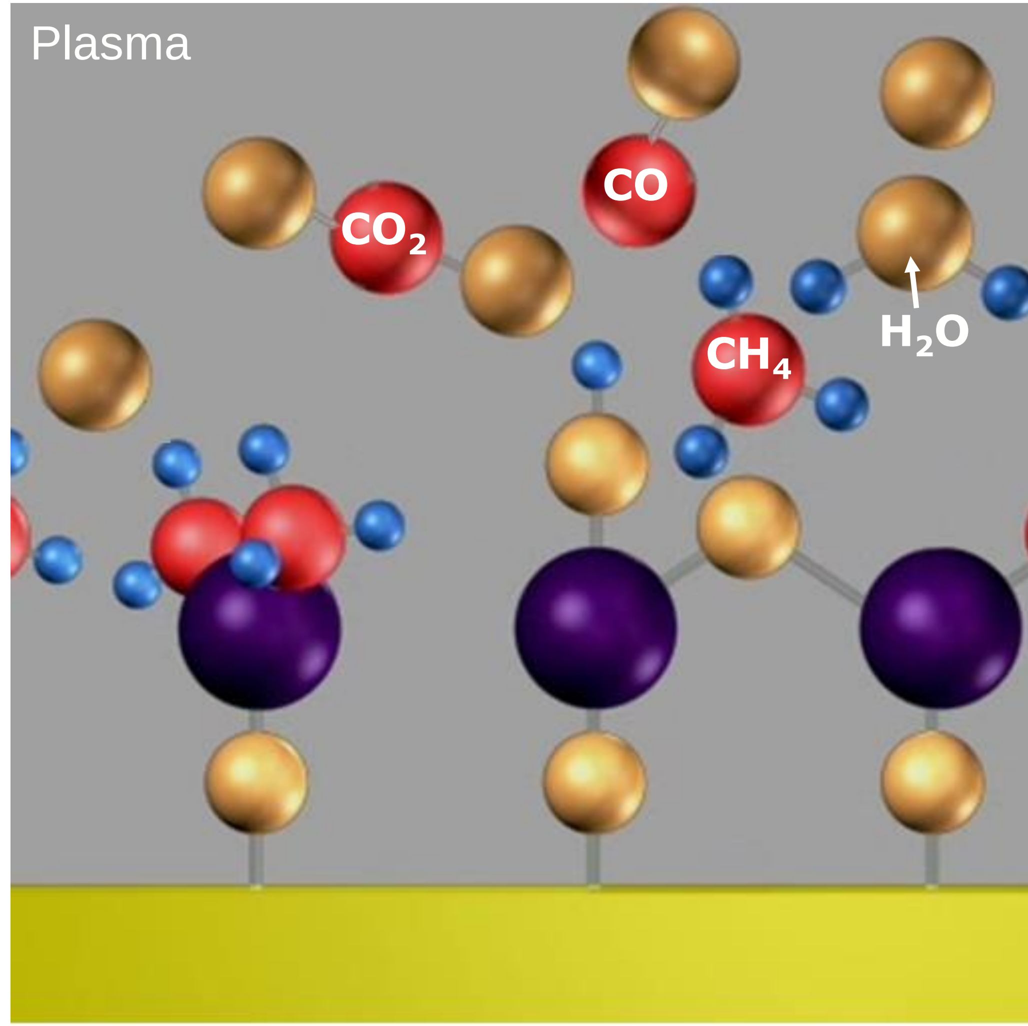
Al_2O_3 ALD Step 3 – Oxidation





Al_2O_3 ALD Step 3 – Oxidation





Plasma vs Thermal Advantages

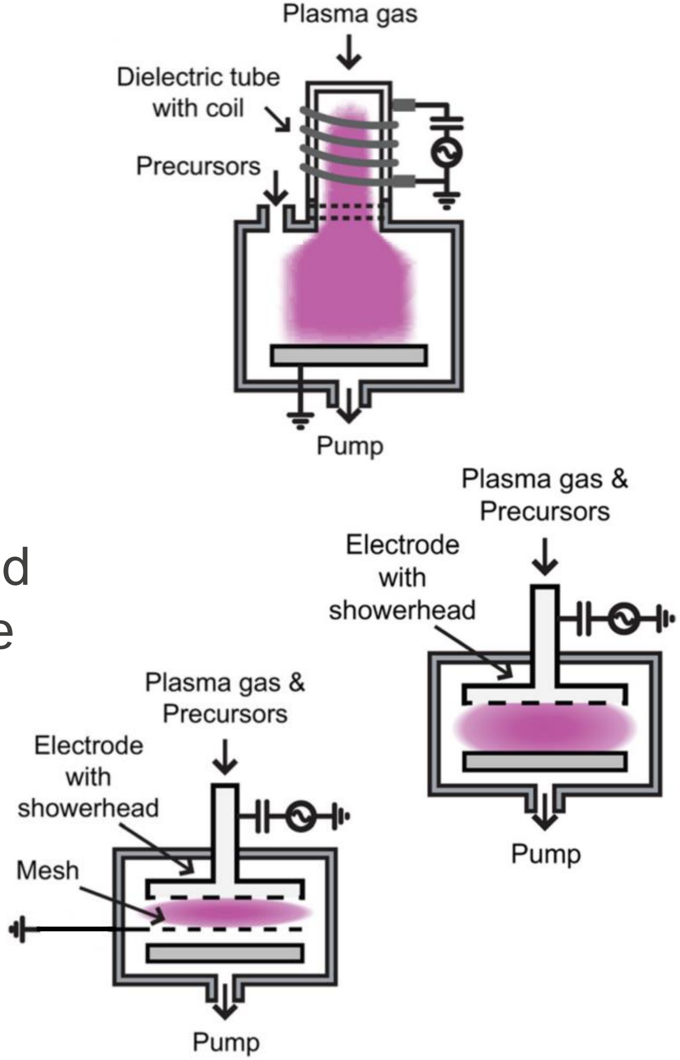
- Lower temperature processing
- Improved film properties
- More precursor/film options
- Reduced purge times
- Reduced nucleation times

Plasma vs Thermal Disadvantages

- Short radical lifetime reduces:
  - spatial uniformity/batch capabilities
  - conformality on high aspect ratio features 20~30:1 maximum
- Chemisorbed precursor or plasma reaction by-products may react with undissociated plasma gas
- Substrate damage
- Cost

PEALD Hardware

- Remote plasma
  - ICP – Veeco – CNT Fiji and other commercial and homemade systems
  - ECR – Hitachi/Picosun
- Direct plasma
  - Common in homemade R&D systems
  - Can be made more “remote” with grounded grid between plasma source and substrate
- Other PEALD-like radical sources
  - Hot-wire
  - Non-ECR microwave plasmas
  - Commercial remote plasma sources



S. B. S. Heil, et al., J. Vac. Sci. Technol. A 25, 1357 (2007).

Veeco | CNT Atomic Layer Deposition

Plasma Gases for PEALD

- Most PEALD processes reported in the literature utilize O_2, N_2, H_2, or NH_3 typically mixed with Ar
- $O_2 + e^- \rightarrow 2O + e^-$ oxides, Pt
- $N_2 + e^- \rightarrow 2N + e^-$ nitrides, metals
- $NH_3 + e^- \rightarrow NH_2 + H + e^-$
  $\rightarrow NH + 2H + e^-$
  $\rightarrow N + 3H + e^-$ nitrides, metals
- $H_2 + e^- \rightarrow 2H + e^-$ nitrides, metals

Less Common Plasma ALD Gases

Gas	Comments
H_2O	Yamagata University has demonstrated room temperature deposition of HfO_2, ZrO_2, and Al_2O_3 with humidified argon plasma
N_2O	Al_2O_3, TiO_2, $AlTiO_x$, HfO_2, ZrO_2, and ZnO have been deposited with N_2O plasma with little to no nitrogen incorporation
CO_2	Al_2O_3, TiO_2 have been deposited with CO_2 plasma with little to no carbon incorporation
D_2	Substituting D_2 plasma has helped elucidate the surface mechanism of Cu deposition from $Cu(hfac)_2$ + H_2 plasma
He	Adding He to the plasma can change plasma density and electron temperature impacting film growth rate and properties
CH_4	Methane plasma admixing has been studied for introduction of carbon to produce TaCN, TiCN, and WCN
CO	Carbon monoxide plasma has been investigated for introduction of carbon to SiO_2
PH_3	GaP has been deposited with trimethyl gallium and phosphine plasma
TMP	Trimethyl phosphate plasma has been studied for Al, Fe, Li, Ti, and Zn phosphate materials
H_2S	Hydrogen sulfide plasma has been studied for the deposition of ZnS, MoS_2, In_2S_3
CH_3NH_2	SiC_xN_y Using Si_2Cl_6 (R. A. Ovanesyan et al. Chem. Matls. 29(15) 2017.)

P. A. Guy, “Alternative Plasma Gas Chemistries for Plasma Enhanced ALD”, ALD 2017 Poster.

~150 PEALD materials reported

Metals 21/20 Ag Al Au Co Cr Cu Fe Ge Hf Ir Mn Mo Nb Ni Pd Pt Ru RuCo Ta Ti W

Oxides 67/35 Al:$BaTiO_3$ Al:WO_3 Al:ZnO **Al_2O_3** AlMgO $AlSi_xO_y$ AlStTiO $AlTi_xO_y$ B:SiO_2 **B_2O_3** **BaO** $BaTiO_3$ **Bi_2O_3** $BiFeO_3$ **CeO_2** **CoO_x** **Cr_2O_3** **CuO_x** **Dy_2O_3** Er:Al_2O_3 **Er_2O_3** **Fe_2O_3** Ga:ZnO **Ga_2O_3** **Gd_2O_3** $GeZrO_2$ $HfAlO_x$ $HfLaO_x$ **HfO_2** $HfSiO_x$ $HfZrO_2$ HfZrSiO IGZO **In_2O_3** InZnO **IrO_2** **La_2O_3** **Li_2O** $LiCoO_2$ $Mg_xZn_{1-x}O$ **MgO** **MnO_x** **MoO_x** MoWO **Nb_2O_5** **NiO_x** **PtO_2** **RuO_2** **Sb_2O_5** **SiO_2** **SnO_2** **SrO** $SrTa_2O_6$ $SrTiO_3$ **Ta_2O_5** $TaNbO_x$ $TaZrO_2$ **TiO_2** TiSiO TiTaO **V_2O_5** **WO_3** **Y_2O_3** YSZ **ZnO** ZnSnO **ZrO_2**

Nitrides 29/16 $Al_xGa_{1-x}N$ AlInN **AlN** BGaN BInN **BN** **Cu_3N** **GaN** **GdN** **HfN_x** InGaN **InN** **MoN** **NbN** **RuN_x** RuSiN RuTaN RuTiN SiAlN **SiN_x** **TaN_x** TiAlN **TiN** TiSiN TiVN **VN** **WN** WSiN **ZrN**

Oxynitrides 6 AlON HfON SiON TiON ZnON ZrON

Phosphides 1 GaP

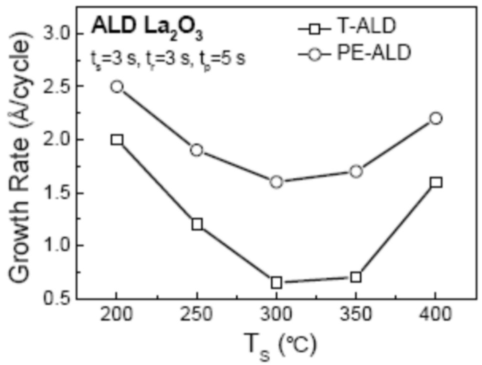
Phosphates 4 AlP_xO_y $FePO_4$ TiP_2O_7 $ZnPO_4$

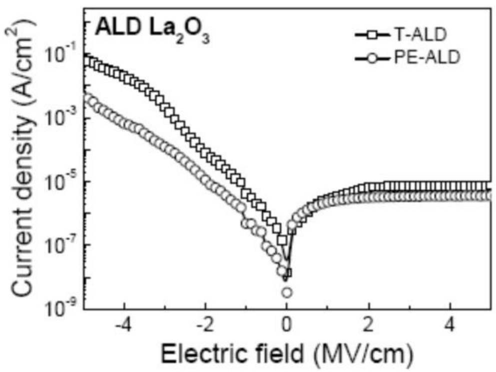
Sulfides 3 In_2S_3 MoS_2 ZnS

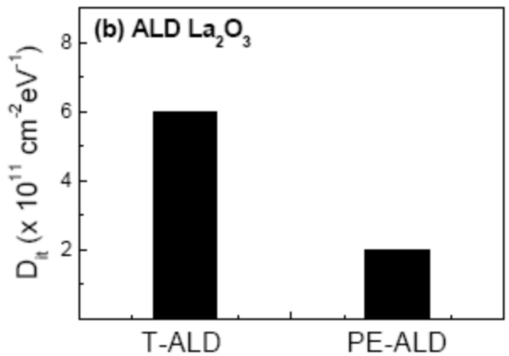
Other 17 GeSbTe Graphene HfOF $In_2(S,O)_3$ Li_2CO_3 LiOH LiPON MoCN Ru-WCN Sb_2Te_3 SiCN SiCOH TaC_x TaCN TiC TiCN WC WCN

Plasma vs Thermal Examples: La_2O_3

- $La(iPrCp)_3 + H_2O$ or O_2 plasma
- Custom remote ICP configuration
- Higher growth rates for PEALD process
- Lower leakage current for PEALD film
- 3x reduced D_{it}



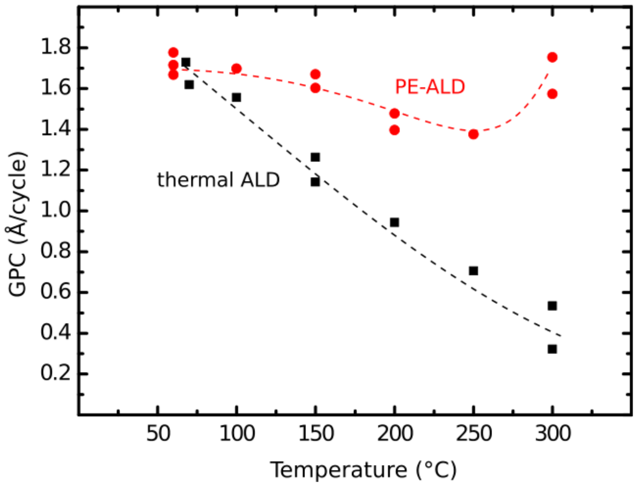




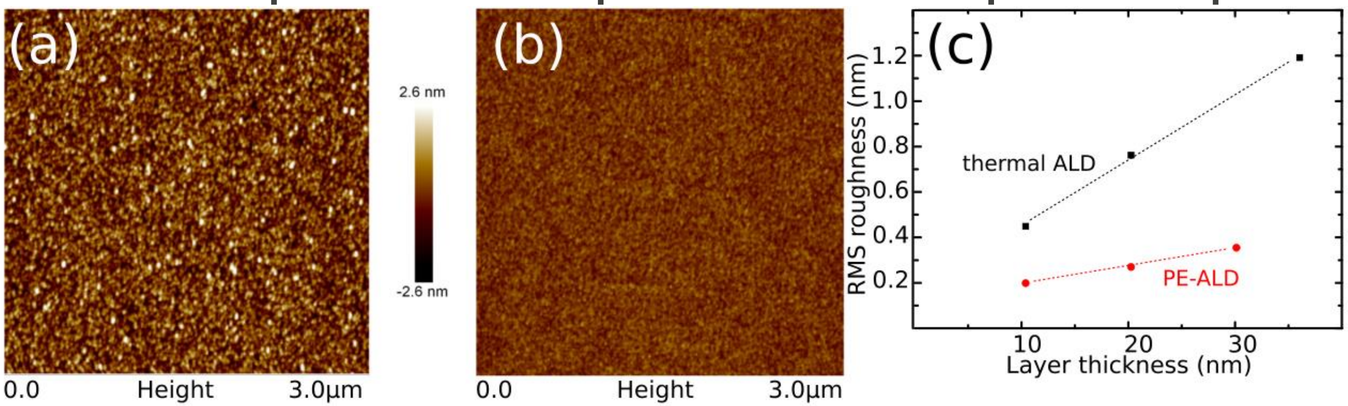
W-H Kim, et al., Thin Solid Films 519 (2010)

Plasma vs Thermal Examples: ZnS

- DEZn +
  - H_2S thermal
  - H_2S/Ar plasma
- Custom remote ICP



- Reduced temperature dependence for plasma process



- Smoother films from PEALD

J. Kuhs, et al., J. Vac. Sci. Technol A 35(1) 2017

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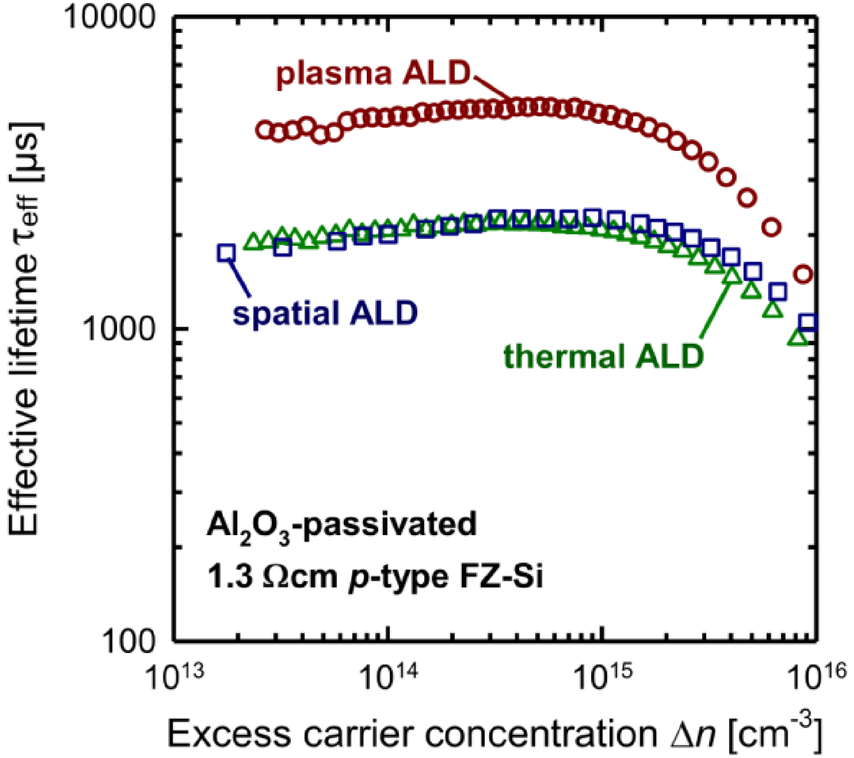
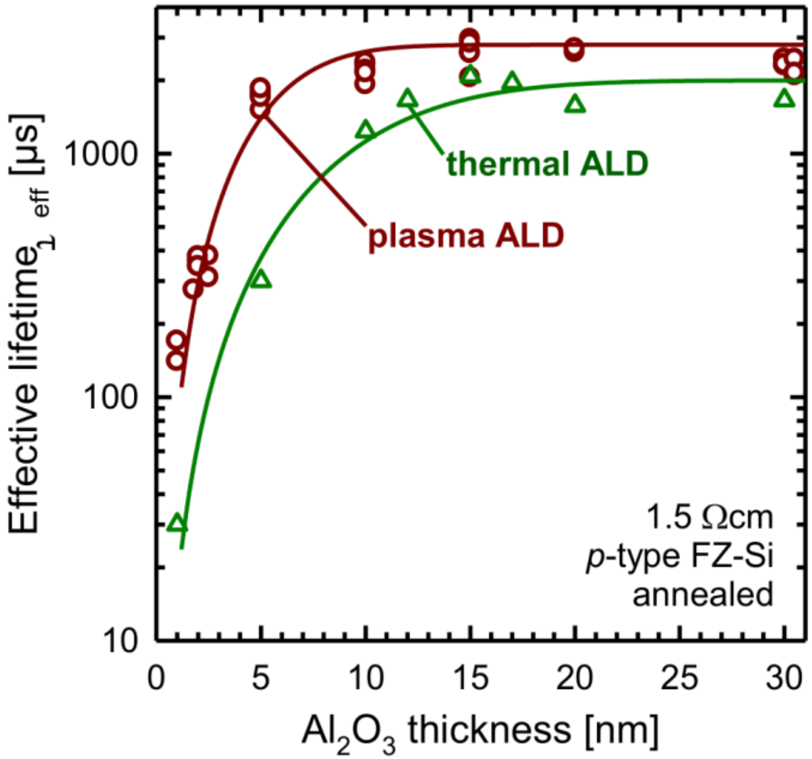
Si Solar Cell Passivation Comparison

- Al_2O_3 – TMA + O_2 plasma

J. Schmidt, et al., 25th Euro PV Solar Energy Conf, 2010.





F. Werner, et al., 25th Euro PV Solar Energy Conf, 2010.

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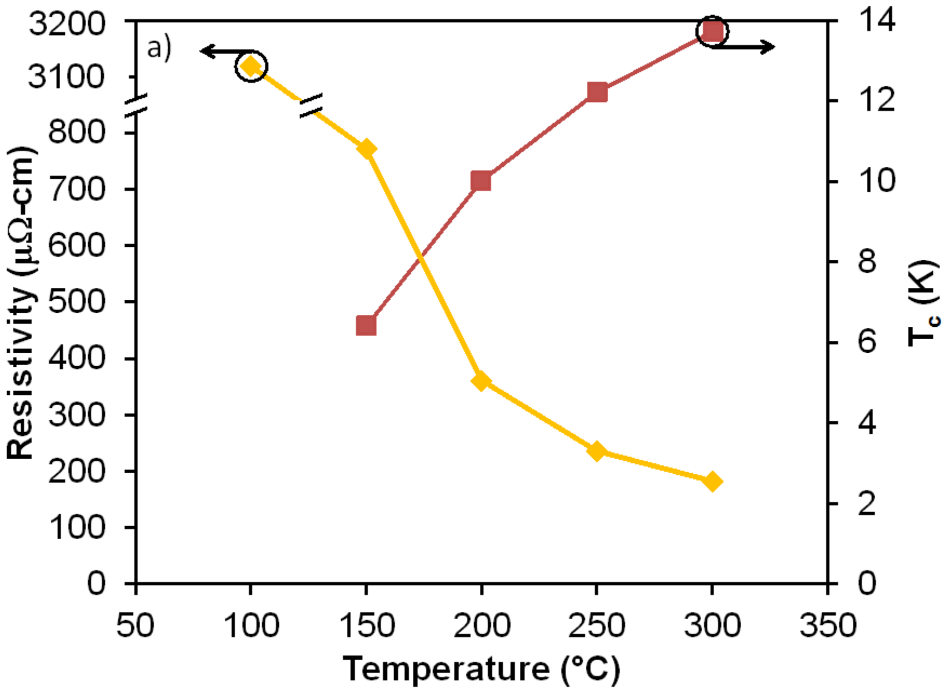
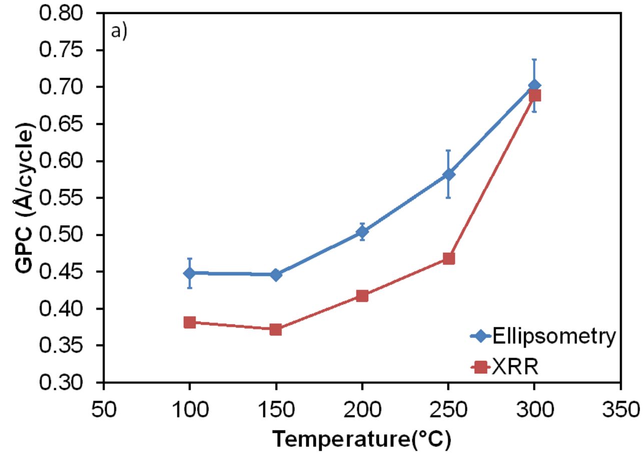
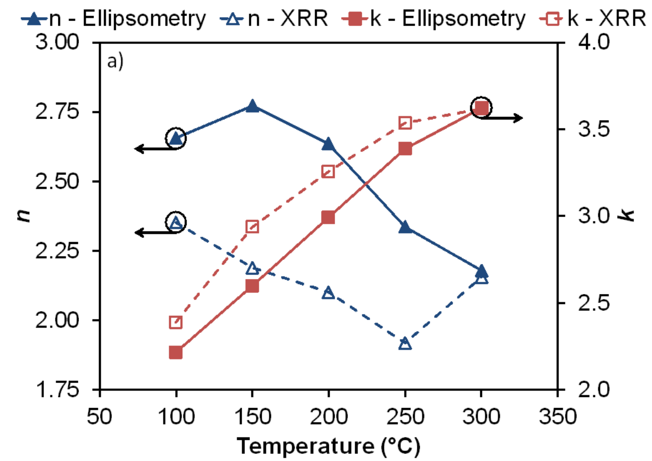
Superconducting PEALD NbN

- Veeco – CNT G2 Fiji
  - TBTDEN, (t-butylimido) tris(diethylamido) niobium(V)
  - H_2/N_2 plasma



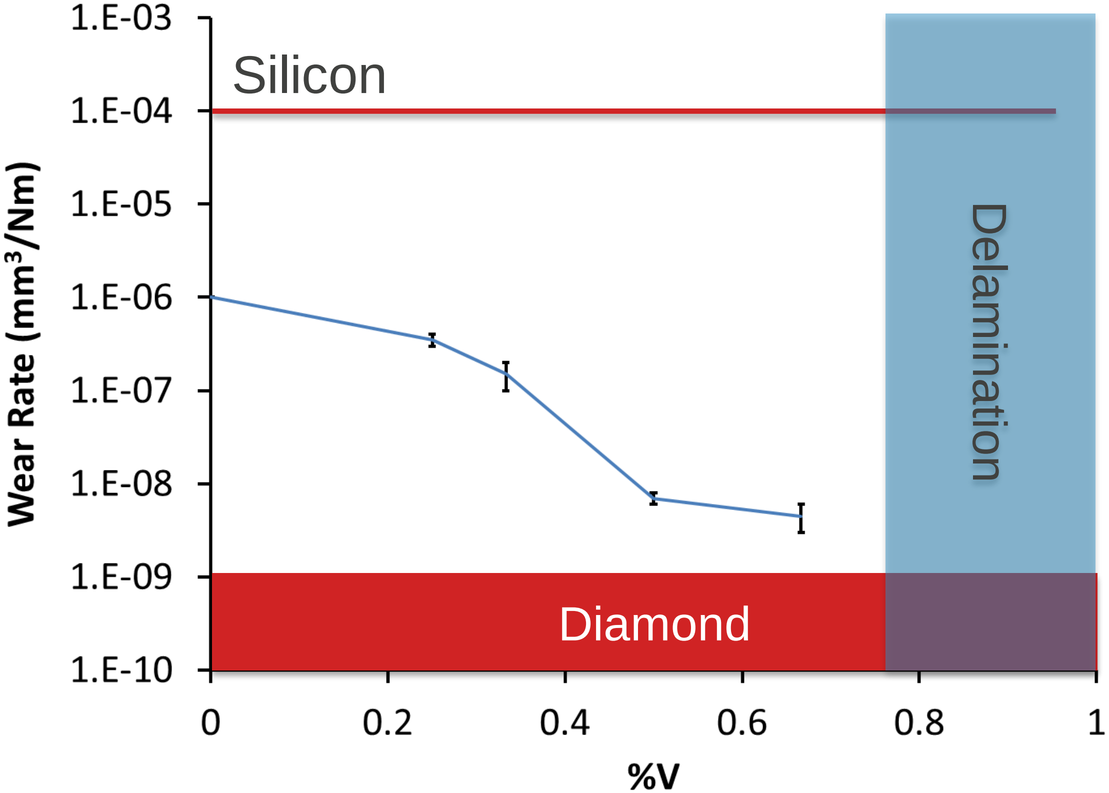


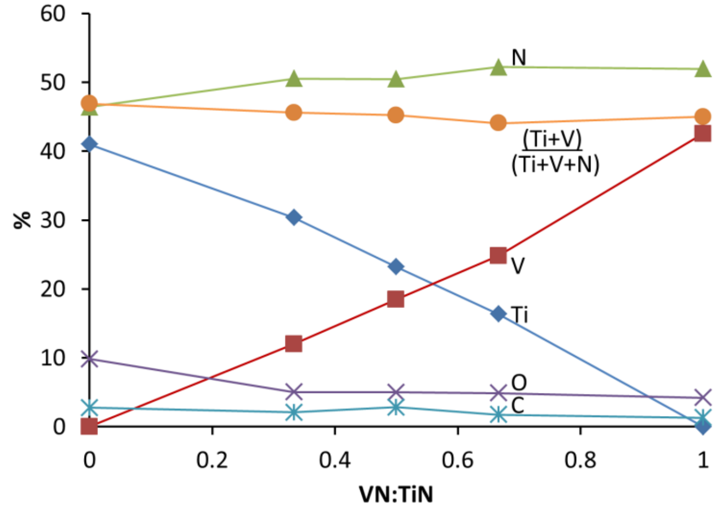


M. J. Sowa, et al., J. Vac. Sci. Technol. A 35(1) 2017.

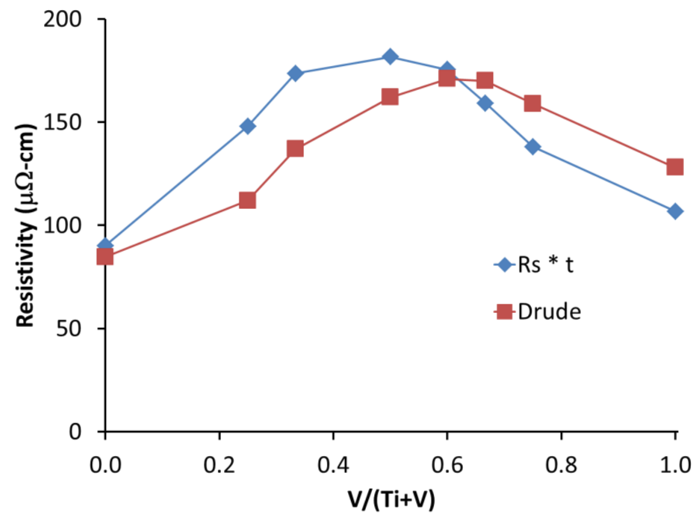
Wear Resistant PEALD TiVN

- Veeco | CNT G2 Fiji, 250˚C, 300W N_2 Plasma, TDMAT, TDMAV
- TiN:VN 1:0, 3:1,2:1, 1:1, 2:3, 1:2, 1:3, 0:1
- TiVN films demonstrated very low wear rates



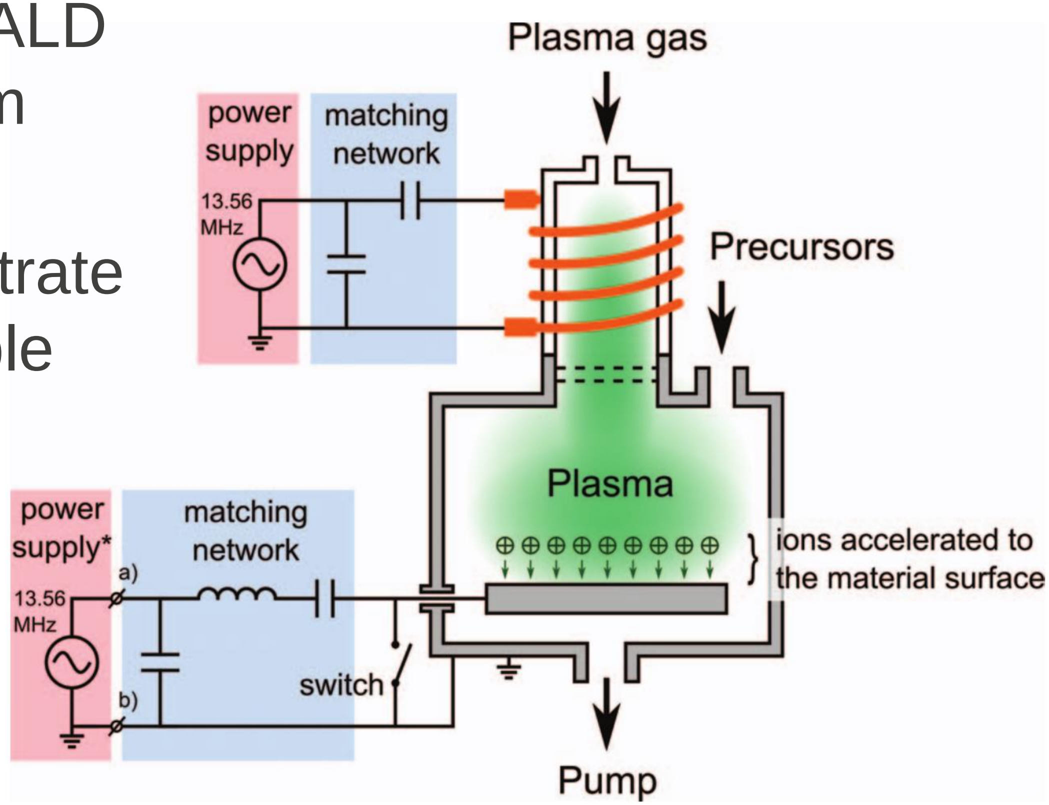


M. J. Sowa, et al., AVS 17th Intl Conf on Atomic Layer Deposition (ALD 2017).



PEALD Substrate Biasing

- It has been recognized that ion bombardment during PEALD affects deposition and film properties
- Applying RF bias to substrate holder enables controllable acceleration of ions into surface of depositing film
- Growth rate
- Stoichiometry, Impurities
- Density
- Crystallinity



H. B. Profijt, et al., Electrochem. Sol. State. Lett. 15(2) 2012.

PEALD Substrate Biasing TiO_2 Results

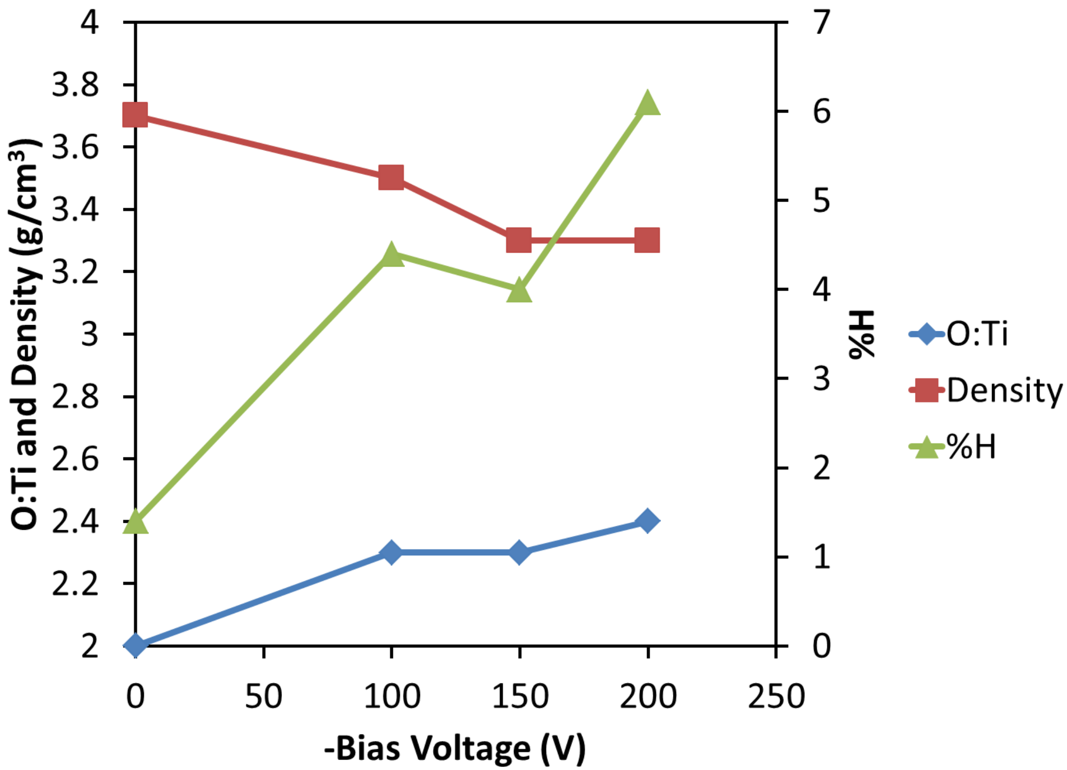
Electrochemical and Solid-State Letters, **15** (2) G1-G3 (2012)
1099-0062/2012/15(2)/G1/3/$28.00 © The Electrochemical Society

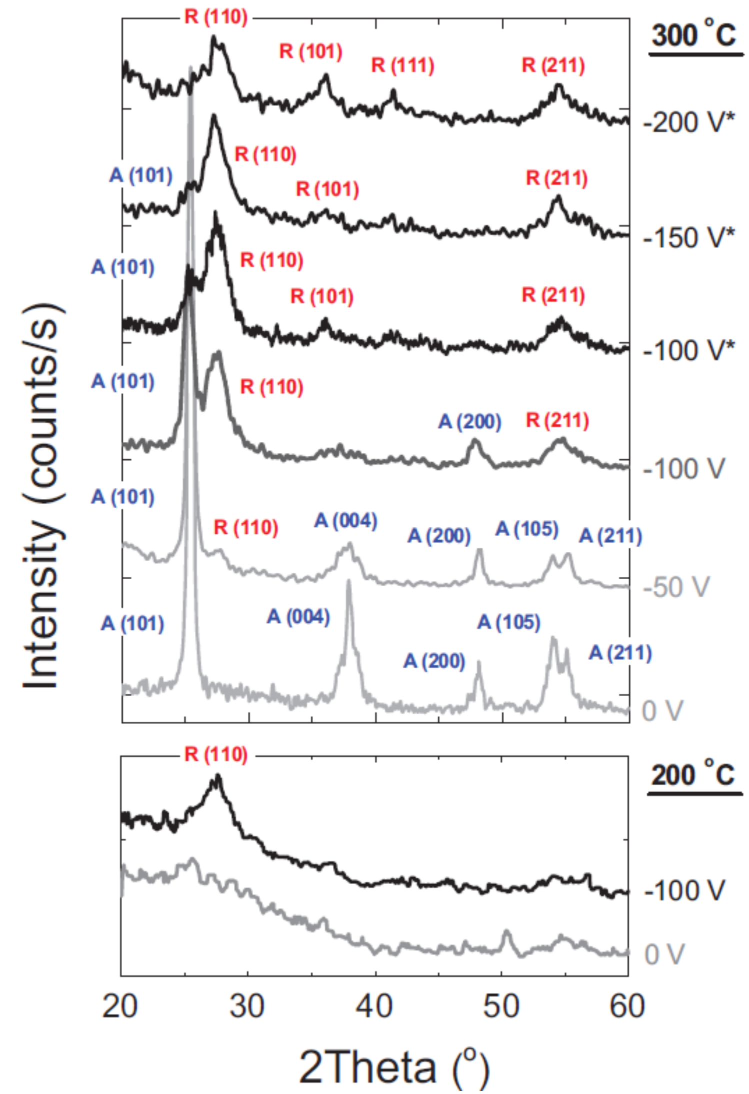
Substrate Biasing during Plasma-Assisted ALD for Crystalline Phase-Control of TiO_2 Thin Films

H. B. Profijt,* M. C. M. van de Sanden, and W. M. M. Kessels**,z

Department of Applied Physics, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

- RF bias affects TiO_2 results





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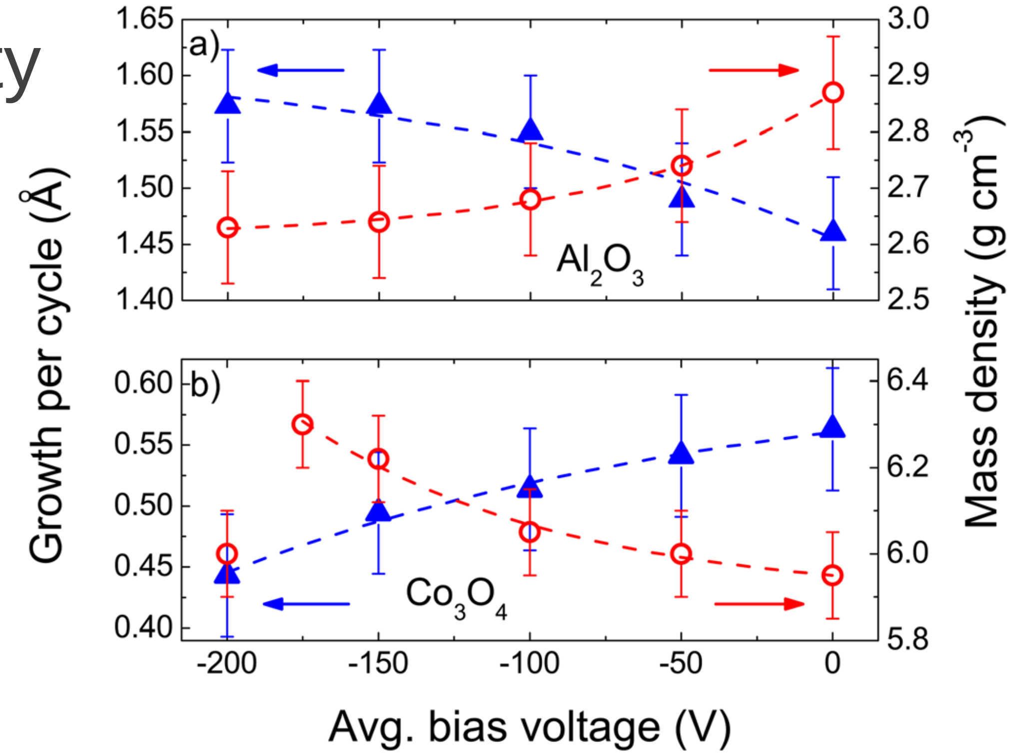
PEALD Substrate Biasing Al_2O_3 and Co_3O_4

- TMA or $CoCp_2$ + O_2 remote ICP plasma
- Growth rate and density show opposite trends
- Al_2O_3 and Co_3O_4 show opposite trends



- Bias option recently added to commercial R&D PEALD systems
- Growing area of research

Electrochemical and Solid-State Letters, **15** (2) G1-G3 (2012)
1099-0062/2012/15(2)/G1/3/$28.00 © The Electrochemical Society

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Other Plasma Uses in ALD

Application	Description	Reference
Substrate Preparation	Ar plasma prep of GaN prior to TMA + $H_2O \rightarrow Al_2O_3$	S.J. Cho, et al., "A study of the impact of in-situ argon plasma treatment before ALD of Al_2O_3 on GaN based metal oxide semiconductor capacitor" Microelec Engr 147 (2015) 277-280
Substrate Preparation	NH_3 plasma nitridation of SiGe prior to TMA + $H_2O \rightarrow Al_2O_3$	K. Sardashti, et al., "Nitride passivation of the interface between high-k dielectrics and SiGe" App Phys Lett108, 011604 (2016)
Doping	In situ H_2/NH_3 plasma doping of DEZ + $H_2O \rightarrow$ ZnO + H_2/NH_3 plasma $\rightarrow$ ZnON	J-F Chien et al., "Local Electronic Structures and Electrical Characteristics of Well-Controlled Nitrogen-Doped ZnO Thin Films Prepared by Remote Plasma In situ Atomic Layer Doping" ACS Appl. Mater. Interfaces, 2012, 4 (7), pp 3471-3475
Doping	In situ NH_3 plasma doping of TMA + $H_2O \rightarrow Al_2O_3$ + NH_3 plasma $\rightarrow$ AlON	Y. J. Cho et al., "Plasma nitridation of atomic layer deposition (ALD) Al_2O_3 by NH_3 in plasma-enhanced chemical vapor deposition (PECVD) for silicon solar cell" Surface & Coatings Technology 307, Part B (2016) 1096 - 1099
Surface Modification	Ex situ H_2 plasma modification of TTIP + H2O $\rightarrow TiO_2$	A. Sasinska et al., "Enhanced photocatalytic performance in atomic layer deposition grown TiO_2 thin films via hydrogen plasma treatment" J. Vac. Sci. Technol. A 33(1), Jan/Feb 2015
Reduction	In situ H_2 plasma reduction of $MeCpMe_3Pt$ + O_2 plasma $\rightarrow$ PtO	A.J.M. Mackus et al., "Room-Temperature Atomic Layer Deposition of Platinum" Chem. Mater., 2013, 25 (9), pp 1769-1774
Oxide Charge Engineering	In situ N_2 plasma nitridation of TMA + $H_2O \rightarrow Al_2O_3$ + N_2 plasma $\rightarrow$ AlON	M.A. Negara, et al., "Oxide Charge Engineering of Atomic Layer Deposited AlO_xN_y/Al_2O_3 Gate Dielectrics: A Path to Enhancement Mode GaN Devices" ACS Appl. Mater. Interfaces, 2016, 8 (32), pp 21089-21094

Final Comments

- ALD is a thin film deposition technique producing high-quality, conformal films over large surface areas at moderate processing conditions
- Supplying plasma generated species for the ALD co-reactant step has been widely studied and has numerous advantages over thermal ALD
- Other applications of plasma to the ALD process have been demonstrated
- Activities in the research community indicate continued strong interest in expanding the ALD application space through incorporation of plasma steps before, during, and after deposition

