Self-assembled monolayers: surface engineering and characterization

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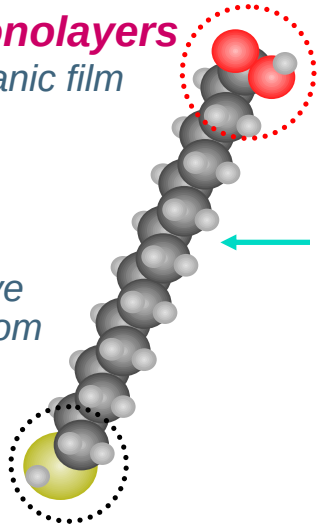
SAMs: surfaces “made-to-order”

Self-assembled monolayers

monomolecular organic film

Self-assembly

spontaneous chemisorption of active surfactant on a solid from gas/liquid phase



Terminal functional group

exposed SAM-gas/liquid interface

methyl, phenyl, amine, carboxylic acid, alcohol, …

Hydrocarbon segments

lateral interactions and tilt to minimise free volume

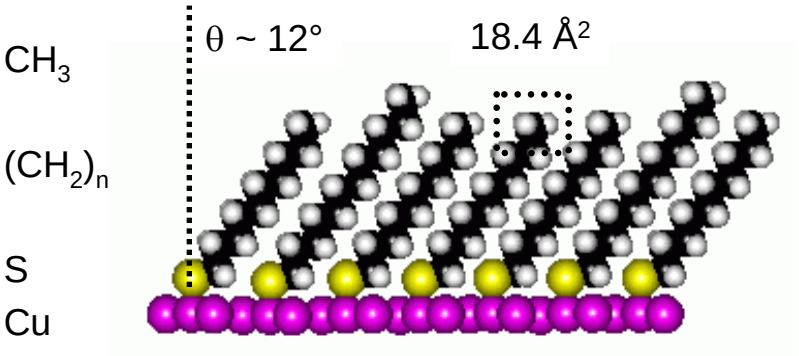
generally alkyl chains with VdWs interactions

Head group

bonding to specific substrate sites

thiol/metals, silane/SiO_2, acid/metal oxide

Organic surfaces ‘made-to-order’



‘pseudo-(100)’ octanethiolate on Cu(111)[1]

Composition controls structure and chemistry

Manipulate atomic scale properties

Engineer surfaces and interfaces

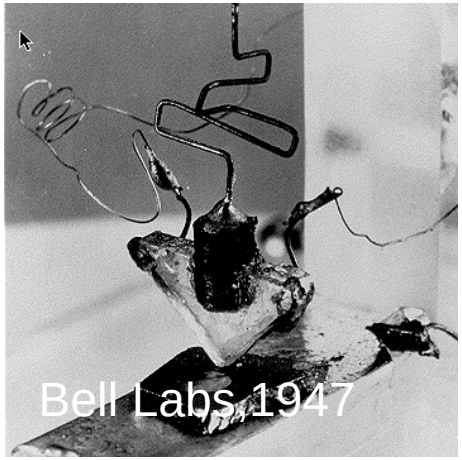
[1]F. Schreiber, Prog. Surf. Sci. **65** (2000) 151

Application of SAMs in Nanoelectronics: surface engineering

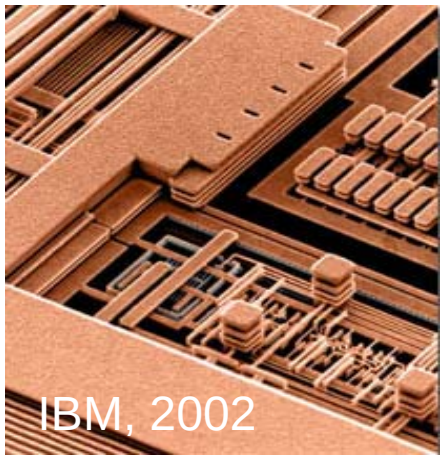
- **ALD of WC_xN_y/various-SAMs** — **Passive**
  - *Atomic layer deposition*
  - *SAM compatibility with ALD*
  - *Effect of SAM termination*
  - *Influence of alkyl chain length*
- **SAMs as Cu diffusion barrier** — **Active**
  - *Previous work*
  - *Adhesion & Cu silicide formation*
- **Characterization of Cu/CO_2H-SAM** — **Characterization**
  - *LEIS: SAM outer most surface*
  - *XPS: SAM-metal bonding*
- **Conclusions**

Atomic Layer Deposition (ALD) for interconnect metallization in IC technology

Shrinking dimensions → Al/SiO_2 → Cu/low-*k* → conformal Cu diffusion barrier → ALD



Scaling requires new materials and processes



- ALD depends on surface chemistry[1] - combination of precursors and their sequence and the type and density of reactive substrate surface sites
- For interconnect metallization - ALD of WC_xN_y as Cu diffusion barrier form on low-*k* substrates[2]

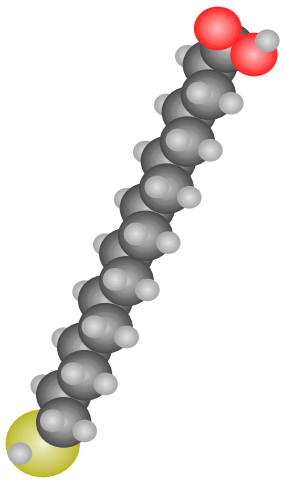
$$WF_6 + NH_3 + B(C_2H_5)_3 + \textbf{\textit{surface groups}} \rightarrow WC_xN_y$$

- Selective (enhance/inhibit) WC_xN_y ALD - identify favourable/unfavourable ***surface groups*** using monofunctionalised surfaces

Use self-assembled monolayers as model substrates for studying ALD processes

[1]Puurunen R.L., J. Appl. Phys. **97** (2005) 121301.
[2]Martin Hoyas *et al.*, J. Appl. Phys., **95** (2004) 381.

Experimental



SAM precursor	$X(CH_2)_nY$
terminal group	$X = CH_3$, Br, CN
CH_2 chain length	n = 7-17
head group	$Y = SiCl_3$

alkyltrichlorosilanes	CH_3-C_n-SAM n=7,9,10,**11**,15,17,21	$\mathbf{CH_3(CH_2)_nSiCl_3}$
bromoundecyltrichlorosilane	Br-C_{11}-SAM	$\mathbf{Br(CH_2)_{11}SiCl_3}$
cyanoundecyltrichlorosilane	CN-C_{11}-SAM	$\mathbf{CN(CH_2)_{11}SiCl_3}$

ALD WC_xN_y:

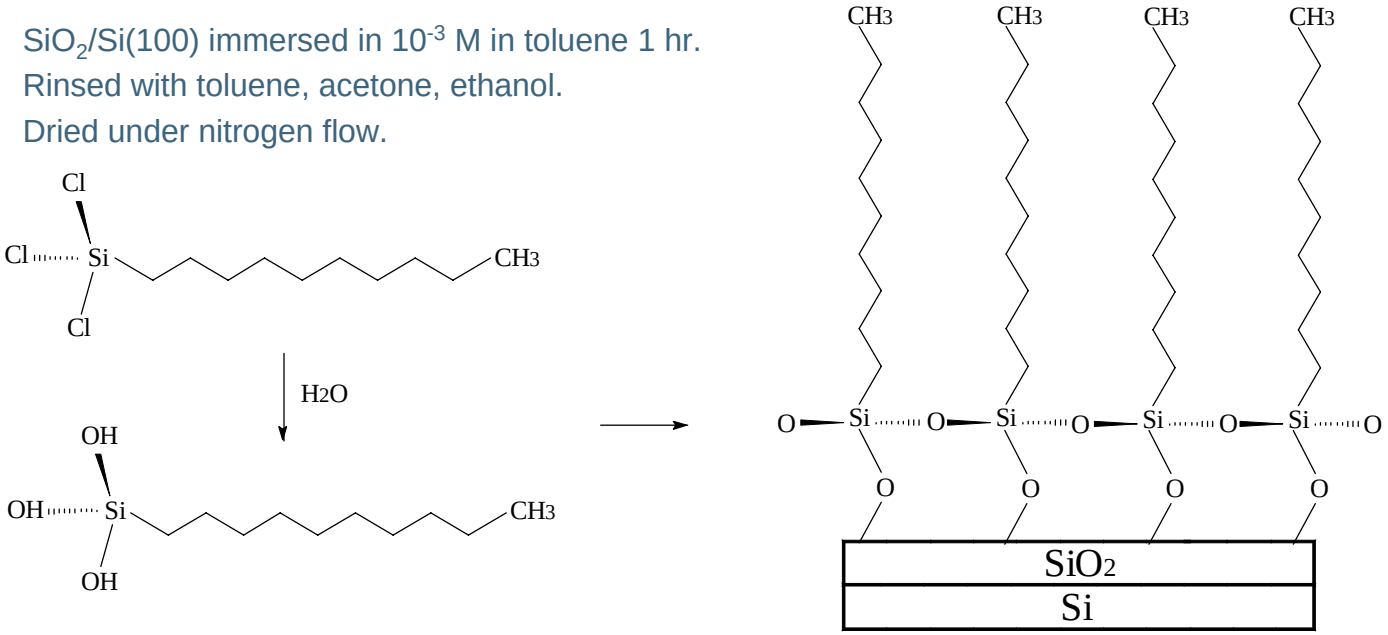
ALCVD™ Pulsar® 2000 reactor integrated with an automated wafer handling platform (ASM Polygon™ 8200). A precursor (mixed with a nitrogen carrier gas flow) pulse sequence of $(C_2H_5)_3B$, WF_6, and NH_3 represents one deposition cycle. Excess precursor gas was removed by flowing nitrogen after each precursor pulse. The deposition temperature was 300ºC.

Analysis:

H_2O contact angle, XPS, TDS, R_s, XRF, ellipsometry, AFM, SEM, EF-TEM, TOF-SIMS, XRR, AES

Experimental

SiO_2/Si(100) immersed in 10^{-3} M in toluene 1 hr.
Rinsed with toluene, acetone, ethanol.
Dried under nitrogen flow.



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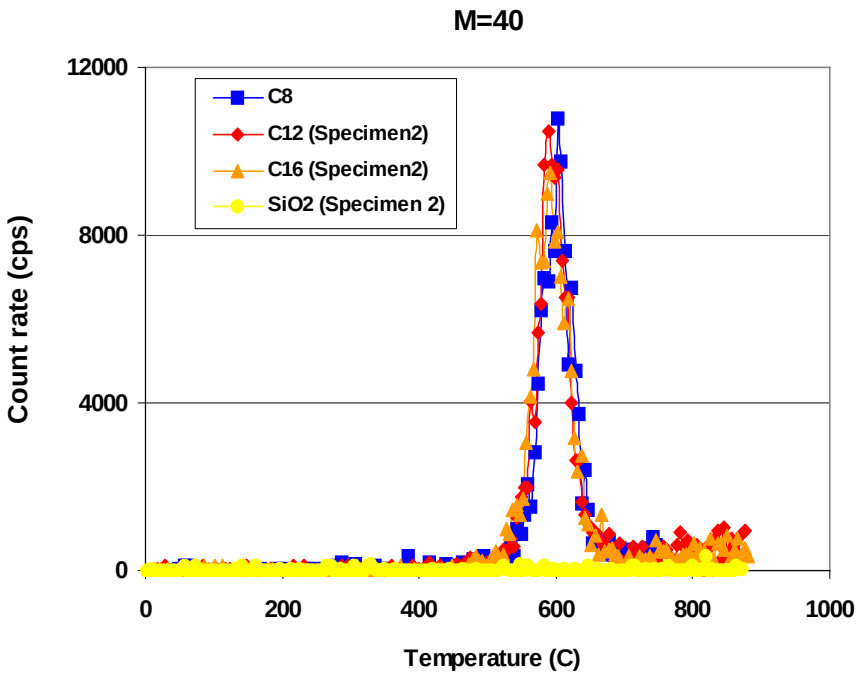
SAM compatibility with ALD: Me-C_n-SAM thermal stability

TDS masses 11-100

Mass Range	n=7	9	11	15	17
26-29	Yes	Y	Y	Y	Y
39-43	Y	Y	Y	Y	Y
47	Y	Y	Y	Y	Y
53-58	Y	Y	Y	Y	Y
66-71	Y	Y	Y	Y	Y
79-85	Y	Y	Y	Y	Y
96-98	Y	Y	Y	Y	Y



All CH_3-C_n-SAMs (n = 7-17) show :

- No water desorption
- Leading edge ~ 500°C
- Maximum 600°C

Decomposition 470-690ºC

For fixed n, substitution of CH_3 with Br or CN reduces thermal stability[2]

Previous EELS study in vacuum of decomposition mechanism for n=3,7,17[1]

- Stable to 470°C
  C-C bond cleavage → HC desorption
- Creates surface CH_3-Si groups to 620°C
- Siloxane head groups to 830°C

[1]Kluth *et al.*, Langmuir, **13** (1997) 3775.

[2]Whelan *et al.*, Mat. Res. Soc. Symp. Proc., **812** (2004) F2.2.1.

SAM compatibility with ALD: WC_xN_y/Br-C_{11}-SAM

Contact angle, XPS, TDS

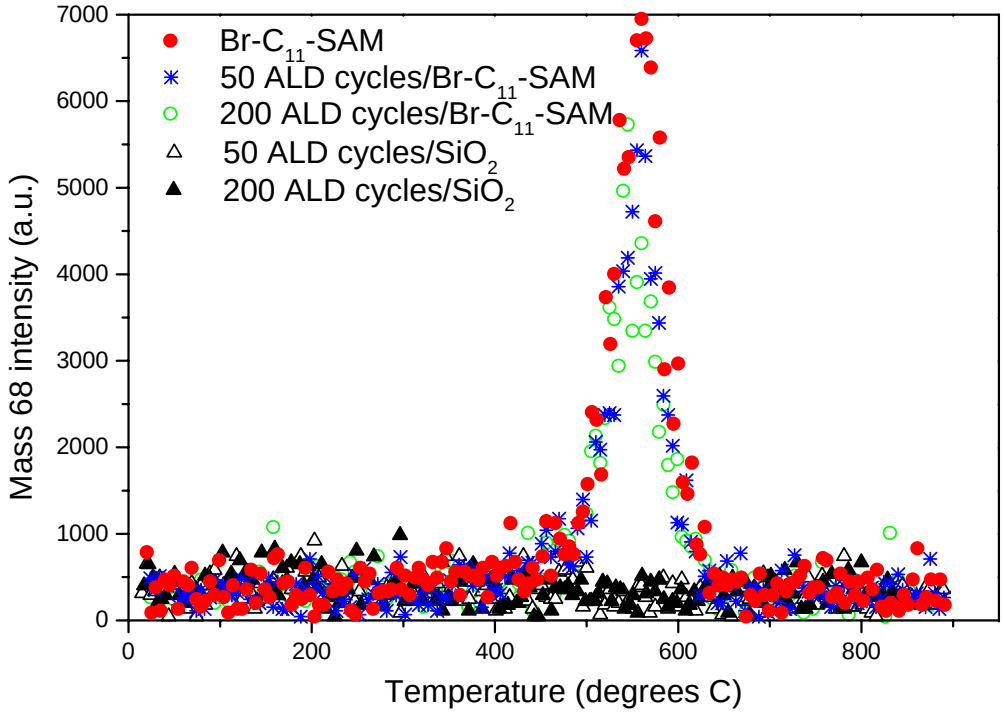
Water contact angle for as-prepared Br-C_{11}-SAM

86.2 ± 1.2° literature

86.6 ± 1.5° experimental

XPS composition analysis of Br-C_{11}-SAM before and after WC_xN_y ALD

ALD cycles	O %	C %	Si_{ox}%	$Si_{substrate}$%	Br %	W %	N %
0	26.77	40.35	11.9	18.8	2.0		
50	33.15	42.2	9.8	13.5	0.46	0.79	
100	41.95	44.08	3.5	4.2		6.23	
200	41.75	41.29				11.13	5.80
500	43.17	36.15				13.21	7.37



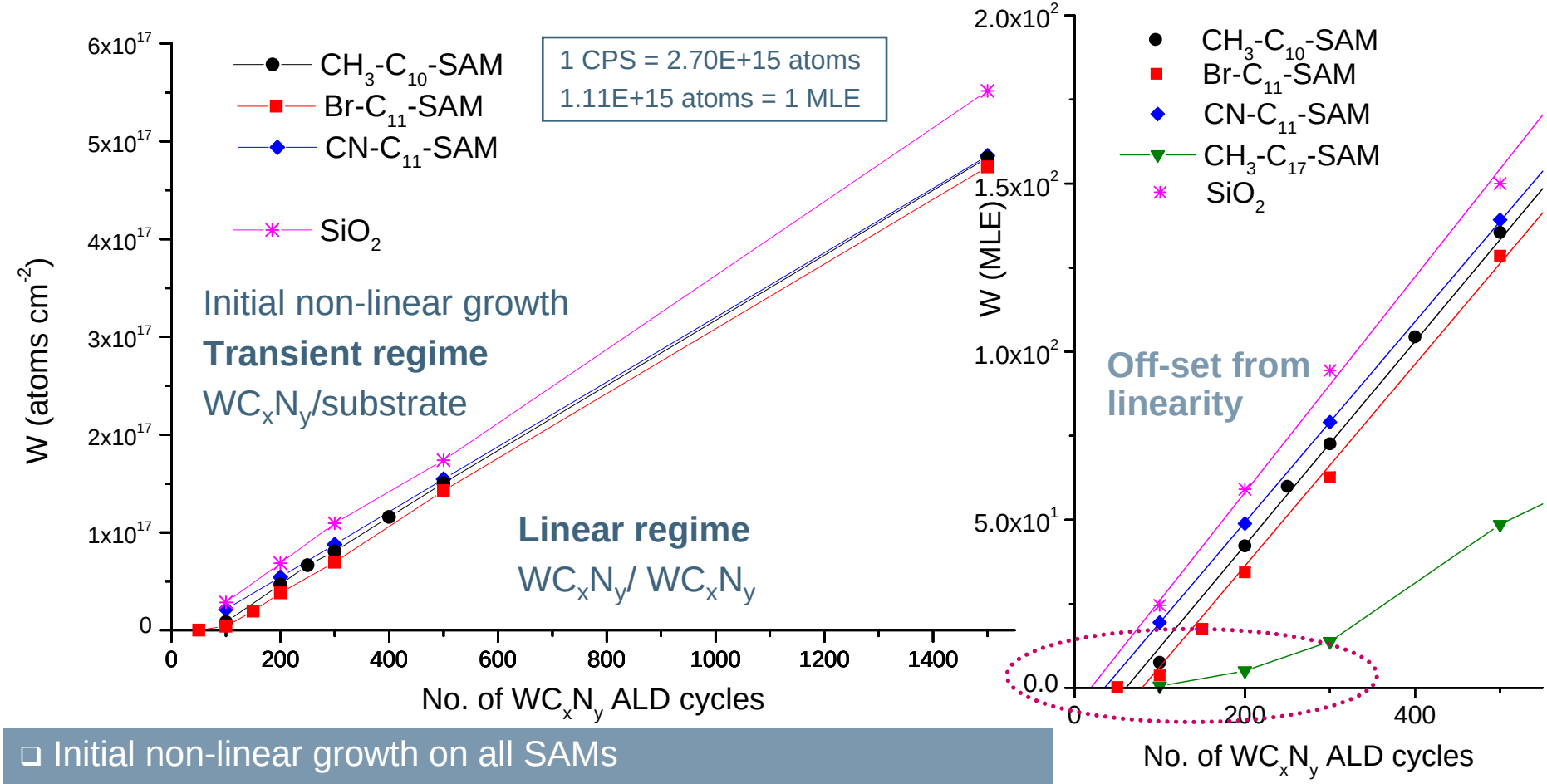
All SAMs show:

- Well-ordered surfaces with expected termination
- No chlorine present
- Desorption maximum 550-600°C
- Survive multiple ALD cycles

Suitable model substrates for studying ALD of WC_xN_y

Effect of SAM termination on WC_xN_y growth: W content

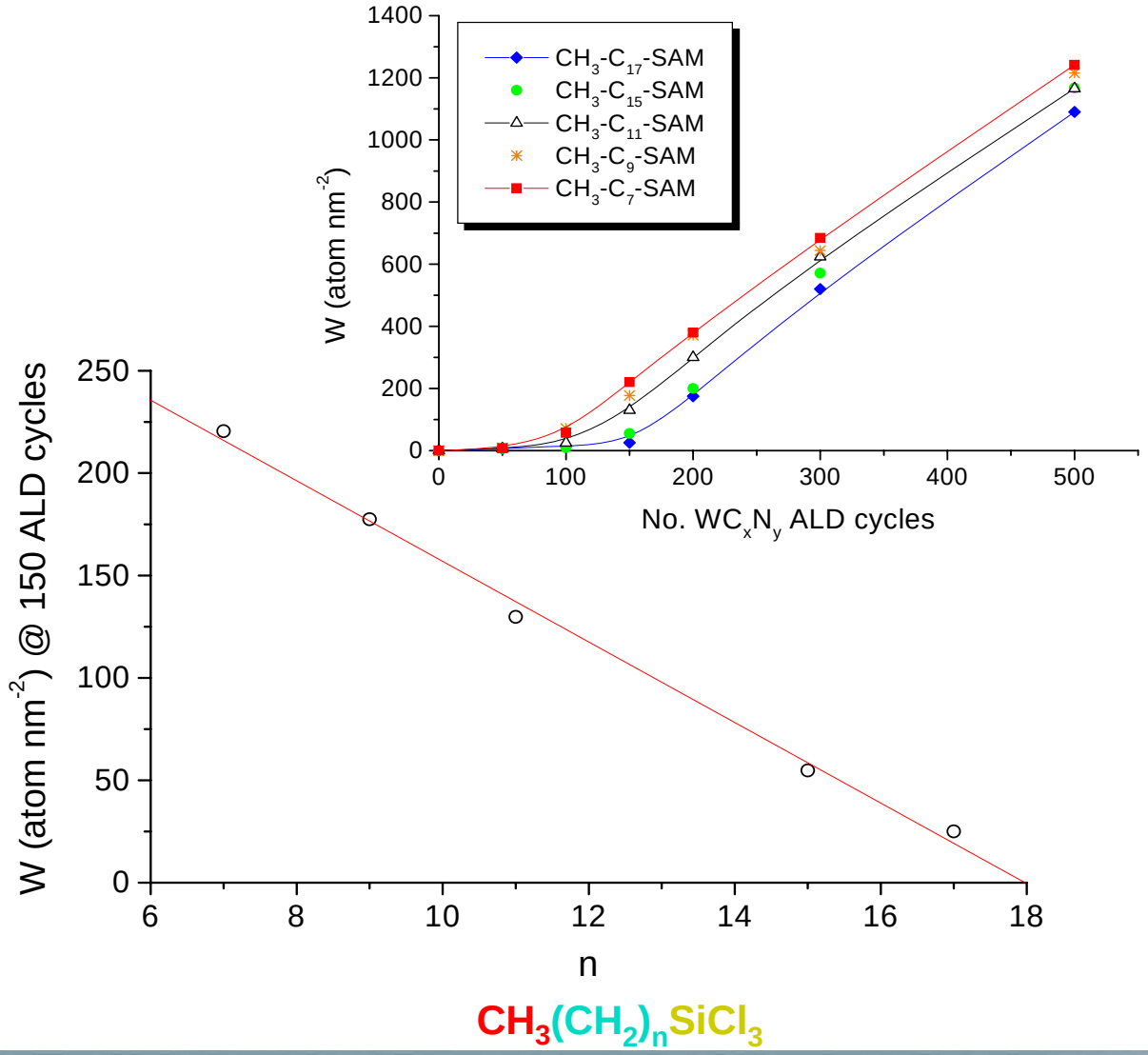
XRF



- Initial non-linear growth on all SAMs
- Linear growth regime from 100-200 cycles for C_{10} & C_{11} SAMs
- Growth on CN-terminated SAM favoured

Effect of terminal group but also influence of alkyl chain length?

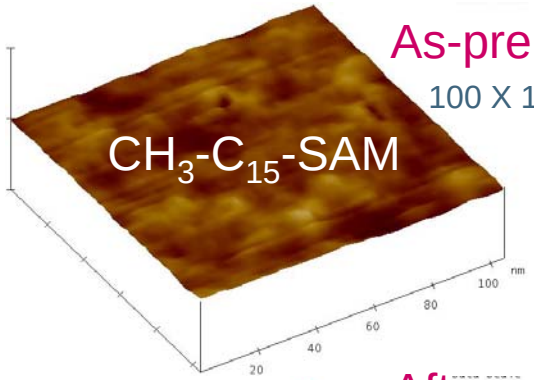
Influence of SAM alkyl chain length on WC_xN_y growth: selectivity **XRF**

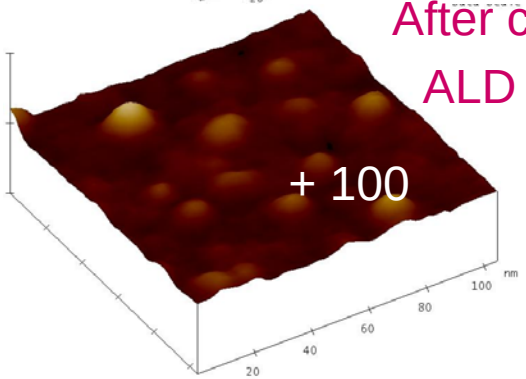


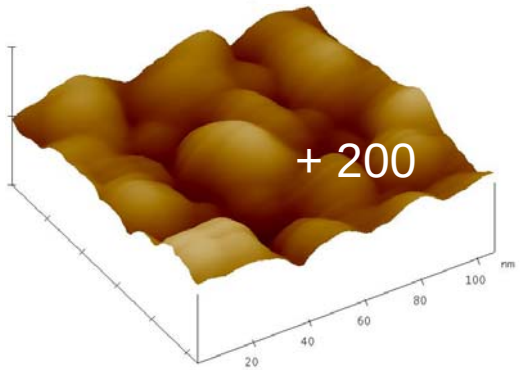
- Selectivity for WC_xN_y growth varies with n
- Offset from linearity increases with increasing chain length
- C_{17} most crystalline with few defects available for metal nucleation – retarding film growth
- C_7 least ordered SAM with higher population of defects available for metal nucleation

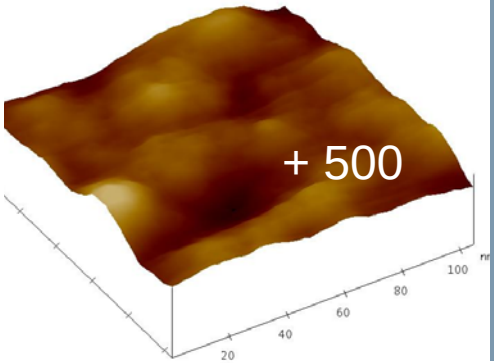
But defects unlikely to be linear over n = 7 to 17

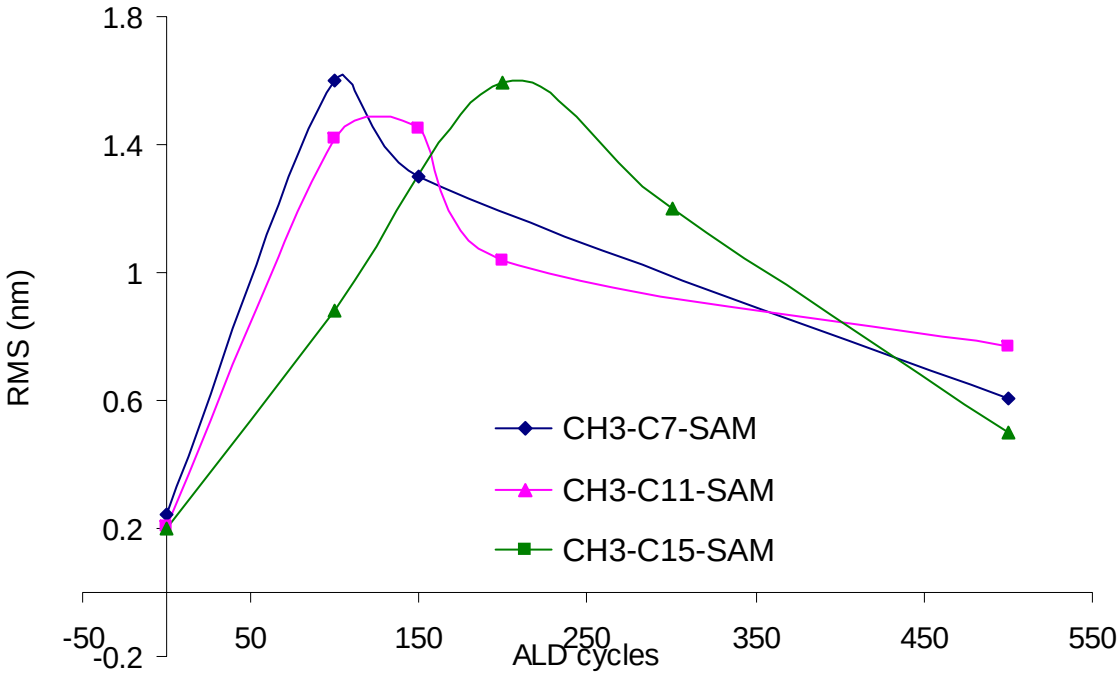
Influence of SAM alkyl chain length on WC_xN_y growth: mechanism **AFM**







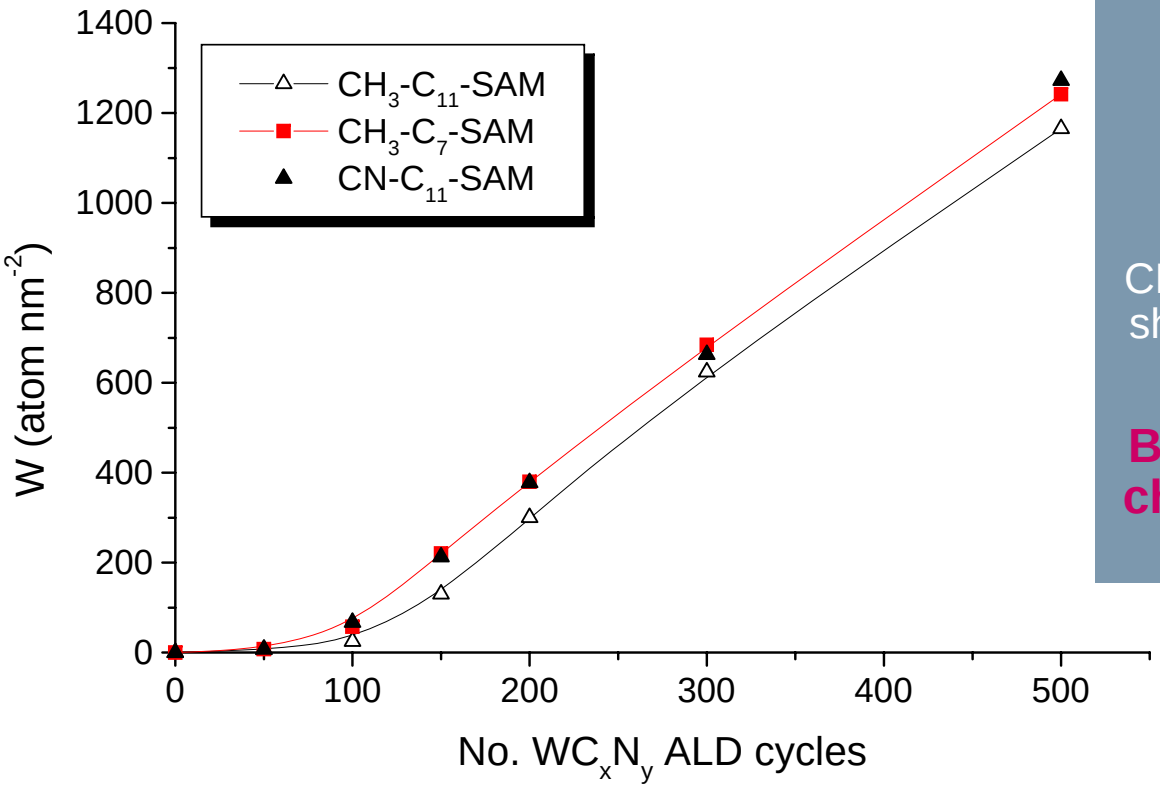




- Islanding growth mechanism
- Constant island density
- Lateral and vertical growth before coalescence

Same for all CH_3-C_n-SAM with chain length dependent offset

Influence of SAM alkyl chain length *vs.* terminal group on WC_xN_y growth: selectivity **XRF**



Selectivity for WC_xN_y growth varies with n BUT influence of n not exclusive

$CN\text{-}C_{11}$-SAM

vs.

$CH_3\text{-}C_{11}$-SAM

$CN\text{-}C_{11}$-SAM similar to $CH_3\text{-}C_7$-SAM shows terminal group enhancement of growth

Both terminal group and alkyl chain length determine WC_xN_y growth behaviour

(1) ALD/SAM: conclusions

- Silane SAMs investigated as model substrates for WC_xN_y ALD for :
  $SiCl_3$ head group, chain lengths (n = 7-17) and terminal groups (CH_3, CN, Br)
- SAMs stable to >470°C and present after multiple 300°C ALD cycles
- SAM termination effects WC_xN_y growth :
  CN-termination favoured
  CN-, Br- & CH_3-terminated C_{10} & C_{11}-SAM *vs.* CH_3-C_{17} SAM
- Selectivity for WC_xN_y growth varies with n due to thickness rather than structural defects within the SAMs

Both terminal group and alkyl chain length determine WC_xN_y growth behaviour

- SAMs provide suitable model substrates for studying metal deposition

Vary substrate structure (alkyl chain) & chemistry (terminal group) to selectively control growth

Application of SAMs in Nanoelectronics: surface engineering

- **ALD of WC_xN_y/various-SAMs** — **Passive**
  - *Atomic layer deposition*
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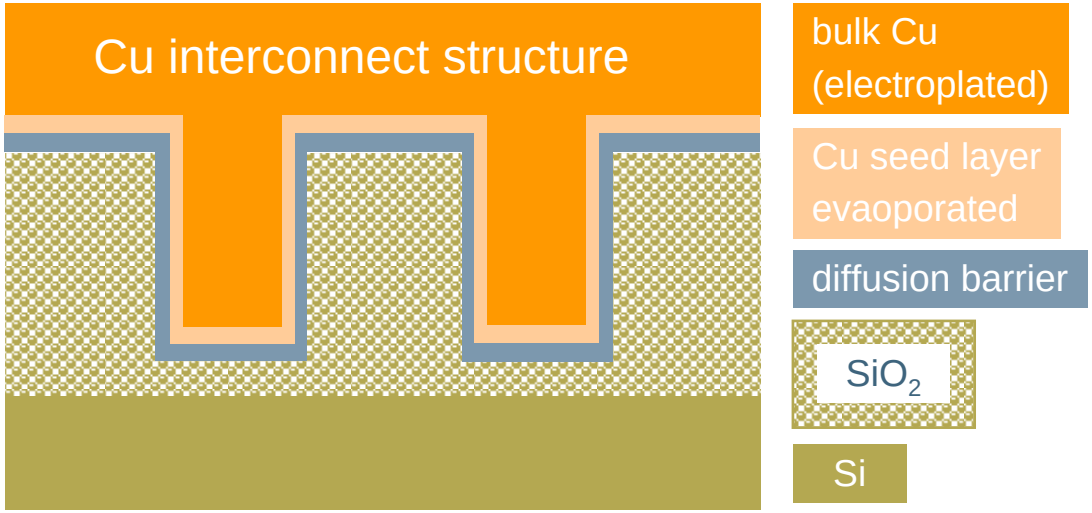
- **SAMs as Cu diffusion barrier** — **Active**
  - *Previous work*
  - *Adhesion & Cu silicide formation*
- **Characterization of Cu/CO_2H-SAM** — **Characterization**
  - *LEIS: SAM outer most surface*
  - *XPS: SAM-metal bonding*
- **Conclusions**

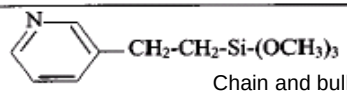
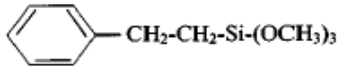
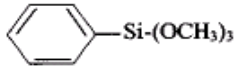
Previous work SAMs as Cu diffusion barrier

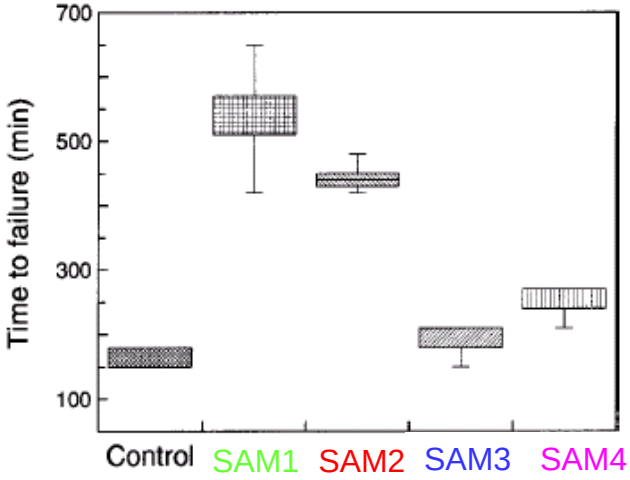
[1]Krishnamoorthy, Appl. Phys. Lett., **78** (2001), [2]Ramanath, Appl. Phys. Lett. **83** (2003)



Cu diffusion barrier properties chain length & terminal group dependent[1]

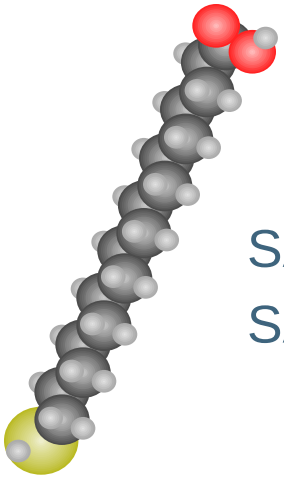
Most promising candidate, SAM-SH, enhances Cu-SiO_2 adhesion & acts as Cu diffusion barrier[2]

Molecule	Chemical formula	IUPAC Name
SAM1		3-[2-(trimethoxysilyl) ethyl] pyridine Chain and bulky head group with reactive heteroatom
SAM2		2-(trimethoxysilyl) ethyl benzene Chain and bulky head group
SAM3	CH_3-CH_2-CH_2-Si-$(OCH_3)_3$	n-propyl trimethoxysilane Chain, no bulky head group
SAM4		phenyl trimethoxysilane No chain, bulky head group



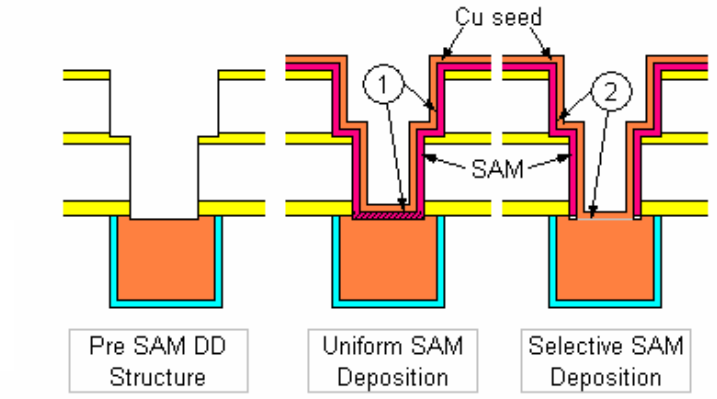
Concept: selecive process for DD integration

C.M. Whelan, V. Sutcliff, U.S. Patent 2006/0128142 A1, European Patent 1 670 054 A1



SAM-$S_{sacrifical}$: $CH_3(CH_2)_9SH$

SAM-$B_{barrier}$: $HS(CH_2)_3Si(OCH_3)_3$



(1) Poor Adhesion: Cu seed to SAM
Questionable electrical conductivity
Good SAM-diel adhesion

(2) No flux divergence
Good Cu-Cu adhesion
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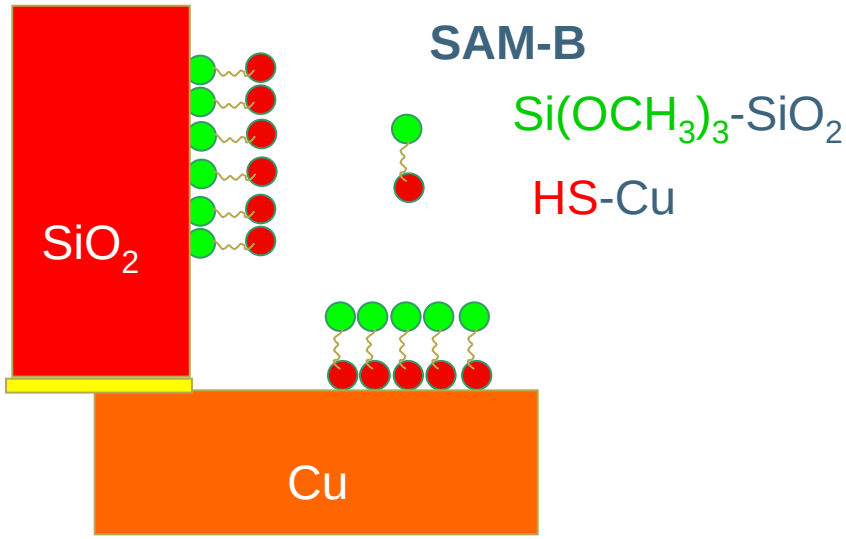
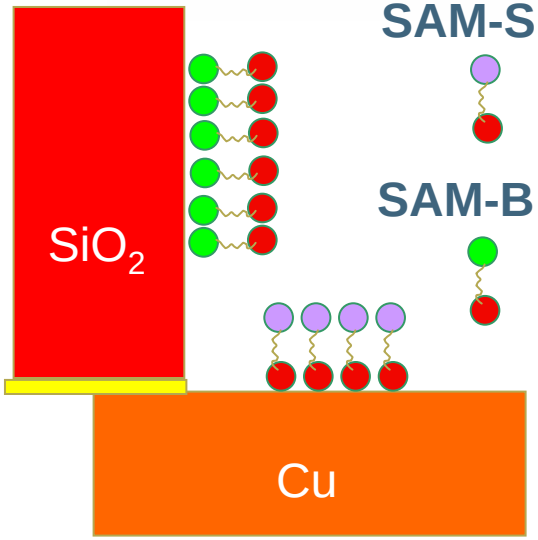


SAM-B

$Si(OCH_3)_3$-SiO_2

HS-Cu



SAM-S CH_3

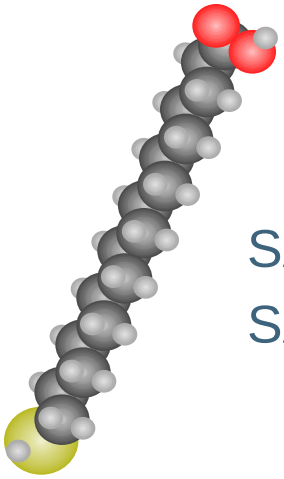
HS-Cu

SAM-B $Si(OCH_3)_3$-SiO_2

HS

Concept: selecive process for DD integration

C.M. Whelan, V. Sutcliff, U.S. Patent 2006/0128142 A1, European Patent 1 670 054 A1



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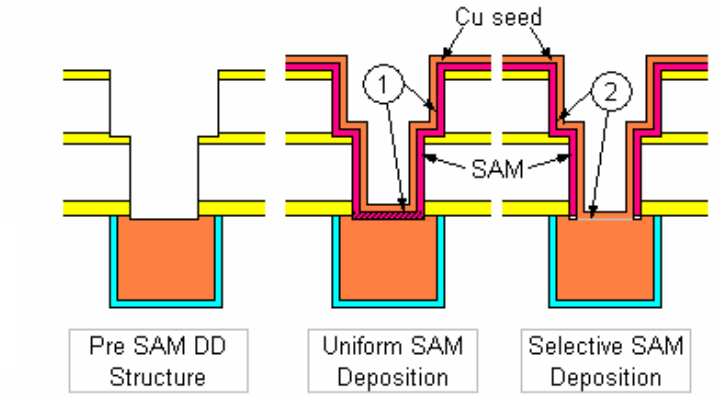

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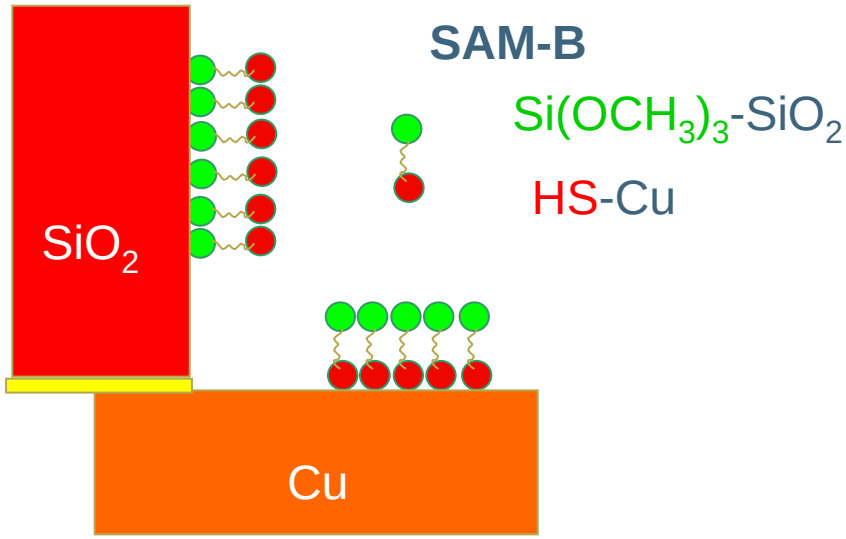

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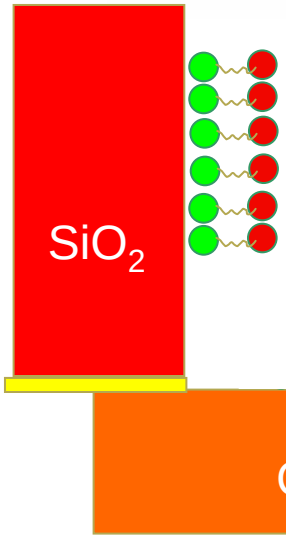


SAM-S

CH_3

HS-Cu

SAM-B

$Si(OCH_3)_3$-SiO_2

HS

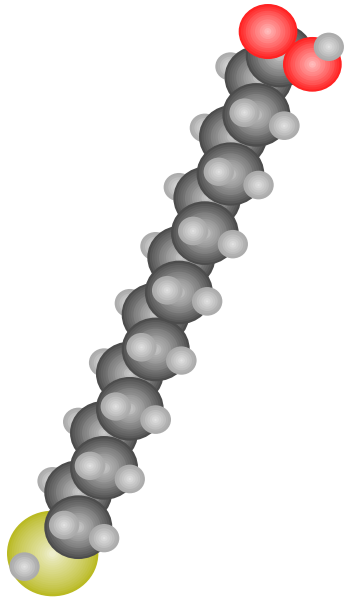
SAM-S thermal release

Assessment of SAMs with systematic variation of molecular structure

Longer chain length $(CH_2)_n$ *for improved film order & Cu blocking efficiency*

New head group $-SiCl_3$ *for improved adhesion, coverage-packing density & thermal stability*

$SH(CH_2)_{n>6}SiCl_3$ not commercially available



Same terminal & head groups but different chain lengths

$CH_3(CH_2)_nSiCl_3$ where n = 7,9,10,11,15,17,21

Same terminal & chain length but different head group

$CH_3(CH_2)_{17}SiX_3$ where X = Cl_3, $Cl_2(OCH_3)$, $(OCH_3)_3$

Same head group & chain length but different terminal group

$CH_3(CH_2)_{11}SiCl_3$ *vs.* $CN(CH_2)_{11}SiCl_3$ *vs.* $Br(CH_2)_{11}SiCl_3$

$SH(CH_2)_3Si(OCH_3)_3$ *vs.* $NH_2(CH_2)_3Si(OCH_3)_3$ *vs.* $C_5H_4N(CH_2)_2Si(OCH_3)_3$

4 points bending probe: fracture surface analysis

SiO_2/CN-SAM/Cu

N 1s peaks → **Cu** and the SiO_2 side

Strong head group-SiO_2 & CN-Cu bonding

SiO_2/Br-SAM/Cu

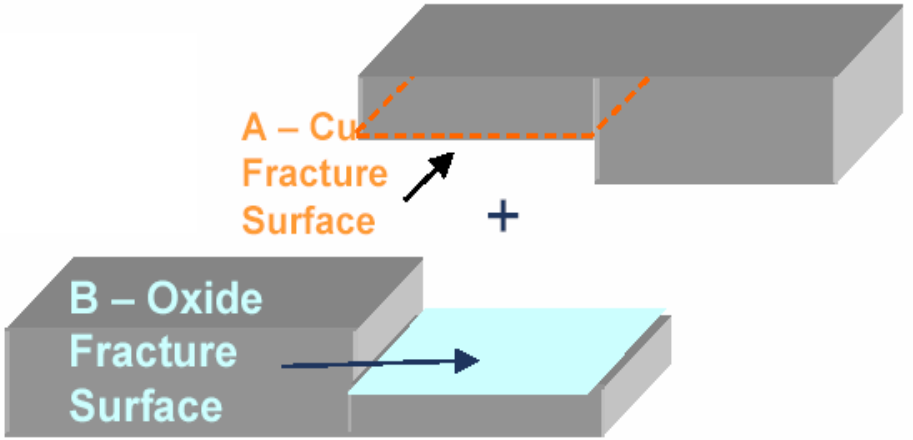
Br 3d peaks → **Cu** side

Weak head group-SiO_2 & strong Br-Cu bonding

SiO_2/SH-SAM/Cu

S 2p peaks → **Cu** side

Weak head group-SiO_2 & strong S-Cu bonding



P.G. Ganesan *et al.,* Mater. Sci. Forum 426-432 (2003) 3487, G. Ramanath *et al.* Appl. Phys. Lett. 83 (2003) 383

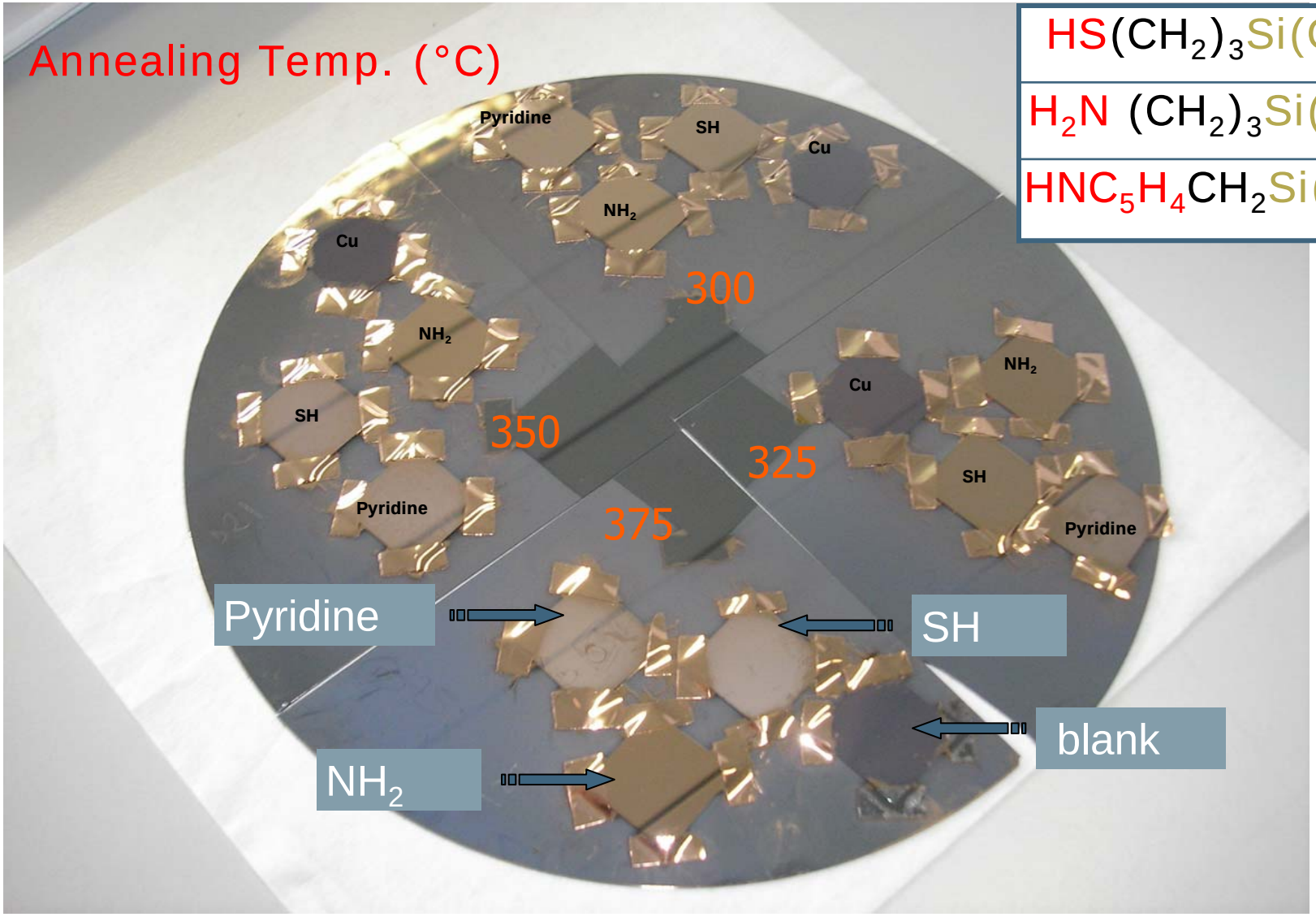
Cu/SH-SAM/SiO_2structures delaminate at SAM/SiO_2 interface

S atoms strongly bound to Cu & $Si(OCH_3)_3$ easily detach from the SiO_2 surface

Cu-SH = Br > CN

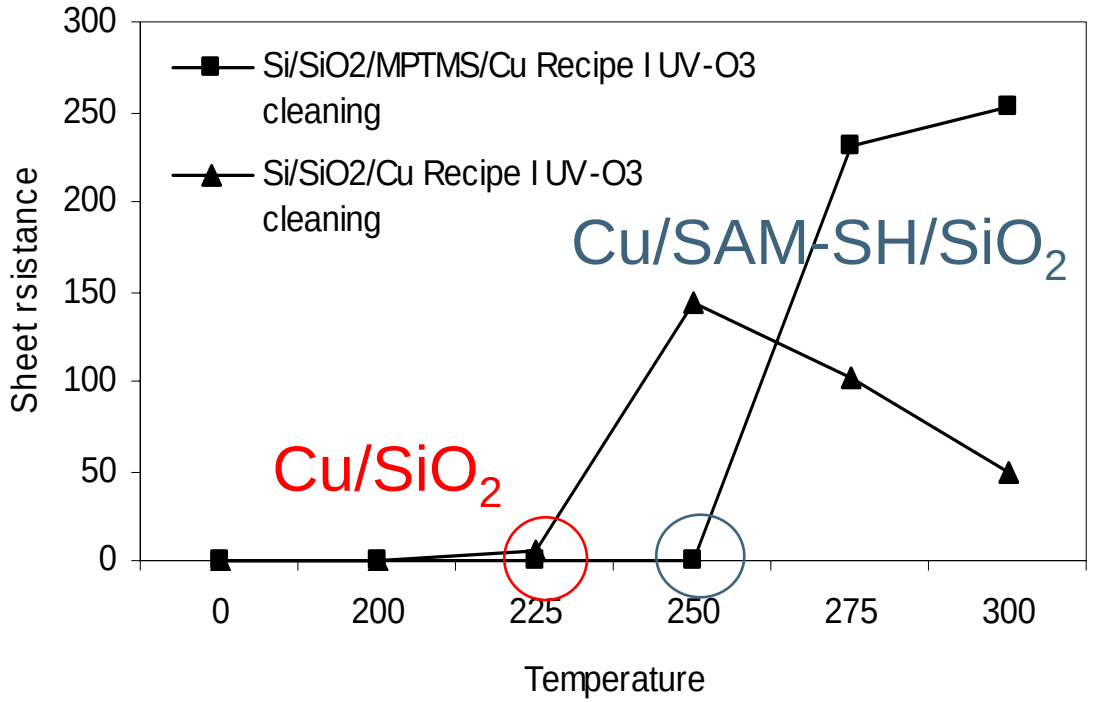
SH-SAM failure at oxide in agreement with literature

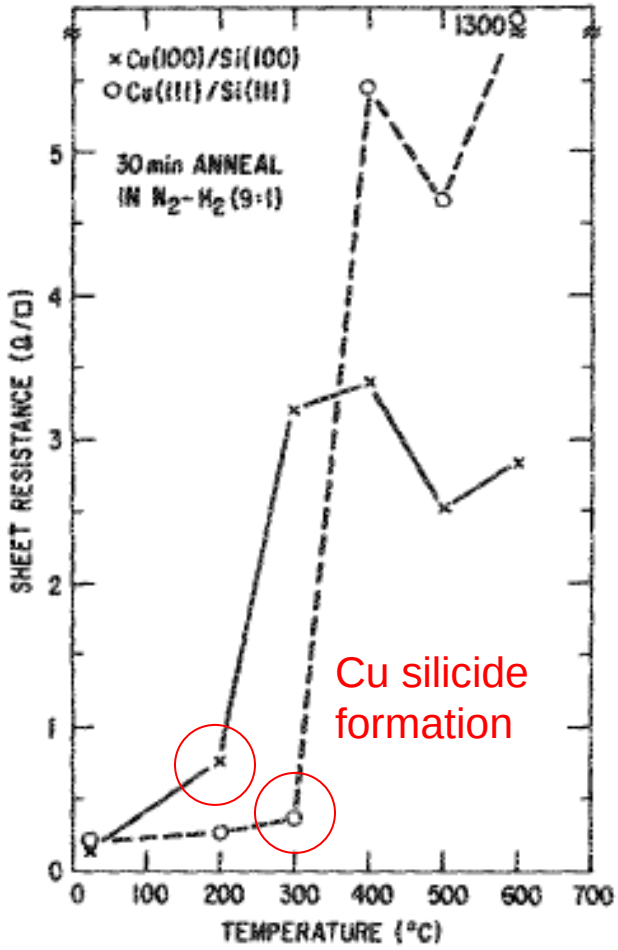
A crude look at Cu/SAM/SiO_2 barrier properties: visual inspection



$HS(CH_2)_3Si(OCH_3)_3$
$H_2N\ (CH_2)_3Si(OCH_3)_3$
$HNC_5H_4CH_2Si(OCH_3)_3$

A crude look at Cu/SAM-B/SiO_2 barrier properties: R_s *vs.* temperature





SAMs compared: adhesion & Cu silicide formation

Sample	Tape test	Sheet resistance ($\Omega/\square$)No	Visual inspection upon anneal
Same CH_3 terminal and $SiCl_3$ head groups but different chain lengths, n= 7-21	Fail	No Cu silicide formation < 400°C	No change
Same CH_3 terminal & chain length, n=17, different head group, $SiCl_3$, $Si(OCH_3)Cl_2$ & $Si(OCH_3)_3$	Fail except $Si(OCH_3)_3$	No Cu silicide formation <400°C but $Si(OCH_3)_3$ >300°C slight inc.	No change
Same $SiCl_3$ head group & chain length, n=11, but different terminal groups, Br, CN, & CH_3	Fail	No Cu silicide formation <400°C	No change
Same $Si(OCH_3)_3$ head group & similar chain length, n=1 or 3, but different terminal groups, NH_2, SH & HNC_5H_4	Pass	Cu silicide formation >300°C* for SH & HNC_5H_4 slight inc.	Darkened except for NH_2

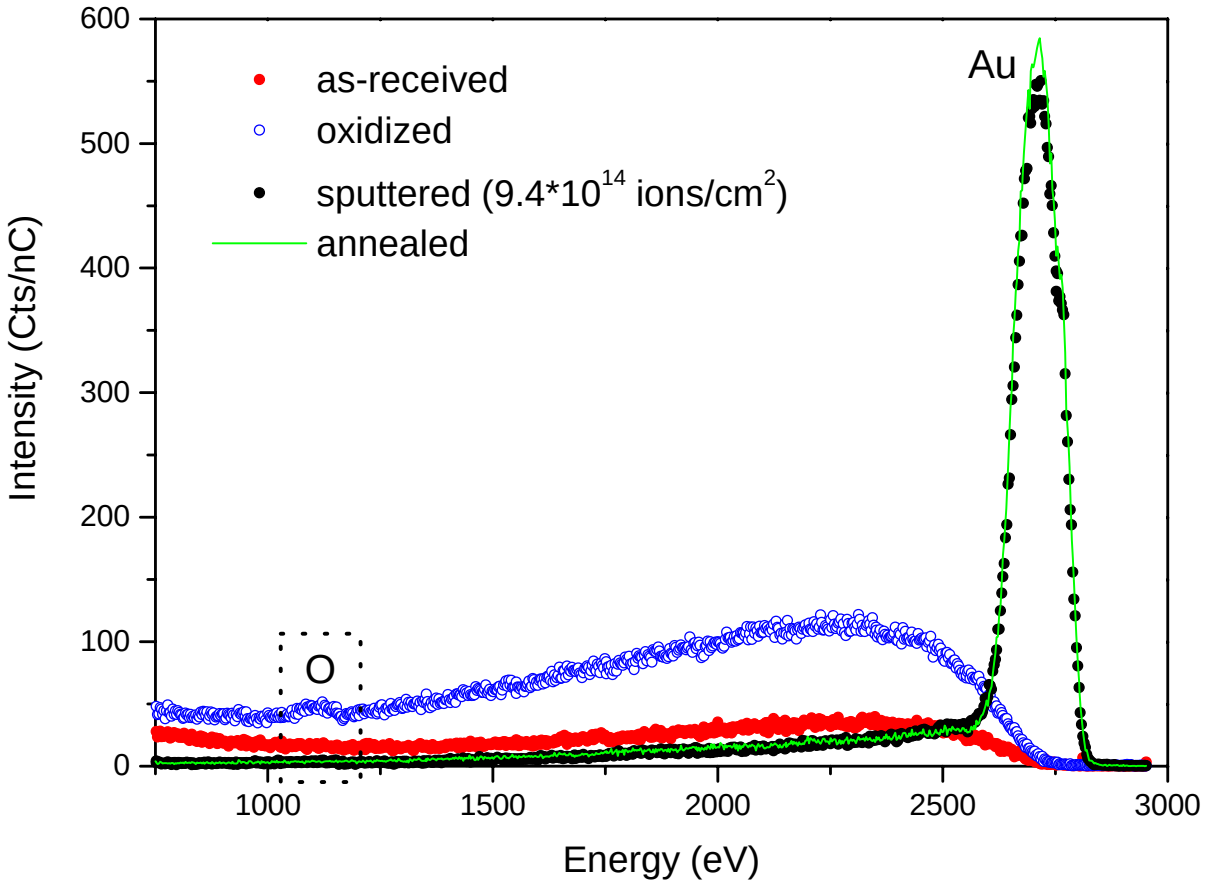
(2) SAMs as Cu diffusion barrier - conclusions

- Molecules with $SiCl_3$ head group show enhanced inhibition of silicide formation (> 400°C) - related to the relatively high thermal stability of the SAM (550-600°C) and dense SAM packing
- No obvious effect of chain length n = 7-21 or terminal group CH_3, Br & CN
- Significant effect from head group, all molecules (including CH_3 terminated) with $Si(OCH_3)_3$ head group pass tape tests - less densely packed SAMs may allow Cu penetration promoting adhesion
- In general, molecules with $Si(OCH_3)_3$ head group, even with reactive terminal groups, show lower inhibition of silicide formation (250-300°C) compared with molecules with $SiCl_3$ head group (>400°C). But adhesion on $Si(OCH_3)_3$ >> $SiCl_3$.

Application of SAMs in Nanoelectronics: surface engineering

- **ALD of WC_xN_y/various-SAMs** — **Passive**
  - *Atomic layer deposition*
  - *SAM compatibility with ALD*
  - *Effect of SAM termination*
  - *Influence of alkyl chain length*
- **SAMs as Cu diffusion barrier** — **Active**
  - *Previous work*
  - *Adhesion & Cu silicide formation*
- **Characterization of Cu/CO_2H-SAM** — **Characterization**
  - *LEIS: SAM outer most surface*
  - *XPS: SAM-metal bonding*
- **Conclusions**

LEIS: preparation of the Au(111) substrate

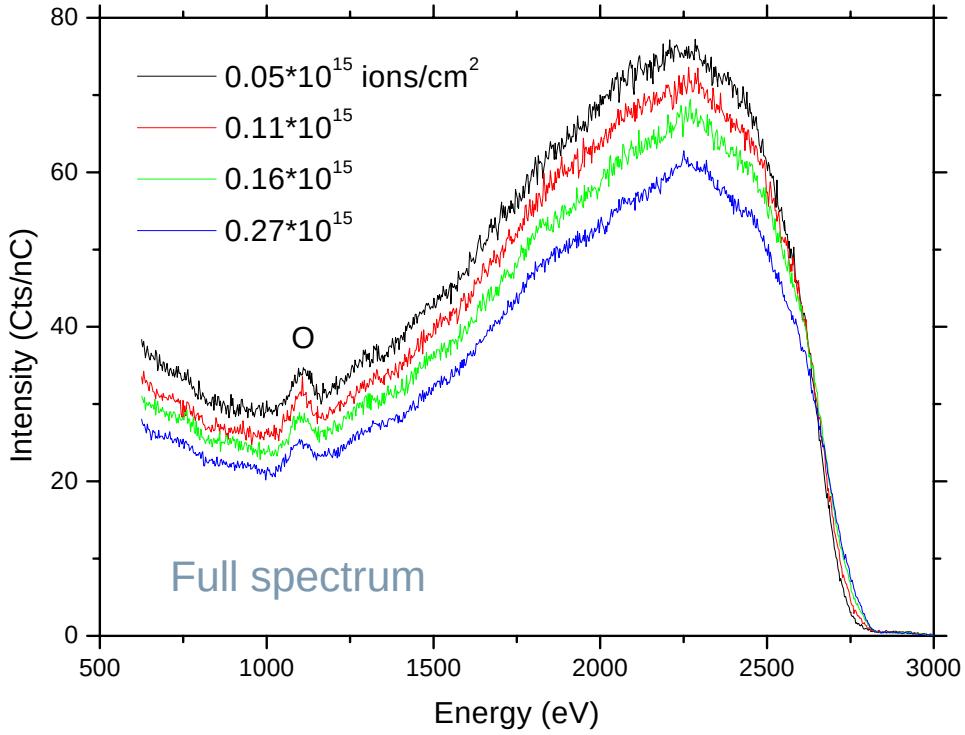


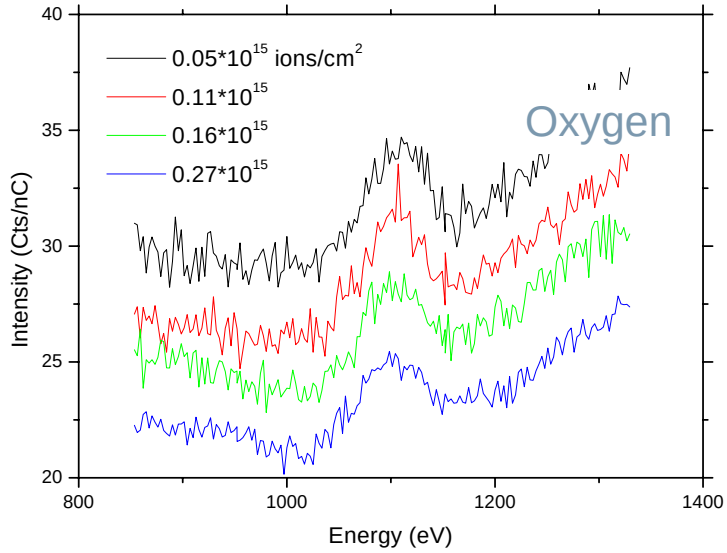
LEIS spectra measured with 3 keV $^{4}He^{+}$ ions from a (111)-textured Au surface as-received, following oxidation treatment with an atomic oxygen source, and after cleaning by $^{20}Ne^{+}$ sputtering cycles and annealing to ~500 K for 30 min.

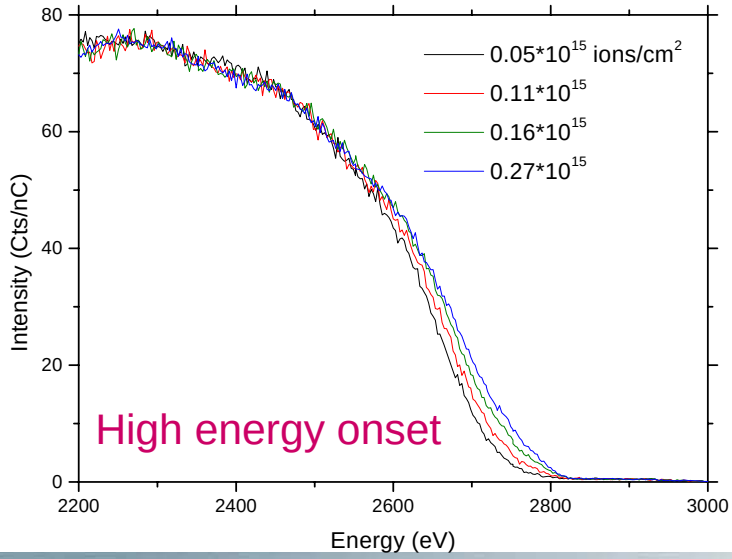
M. de Ridder and H.H. Brongersma

Calipso B.V., Eindhoven, The Netherlands.

LEIS: gas phase adsorption of 3MPA



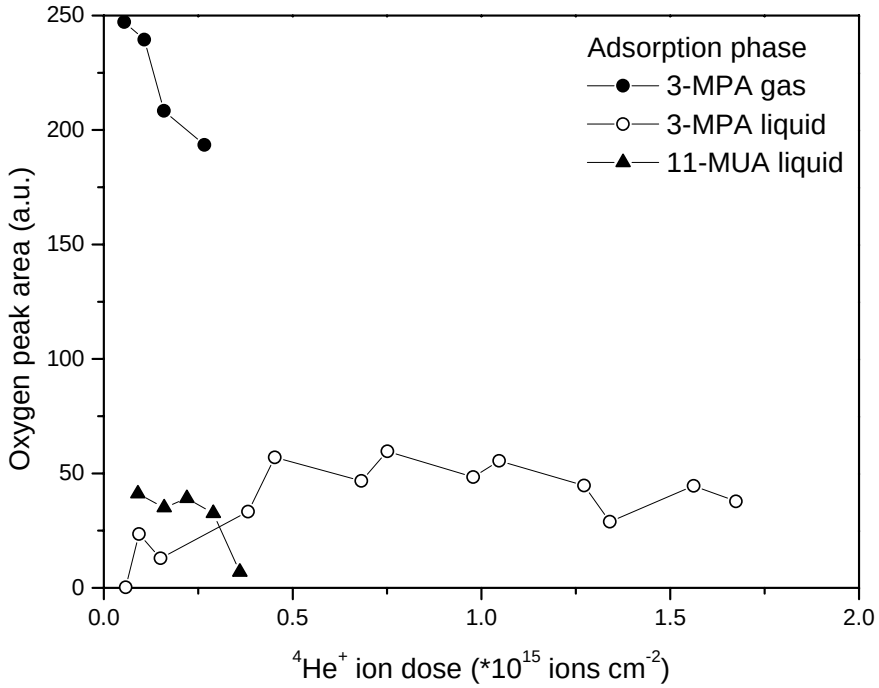




LEIS spectra measured with 3 keV $^4He^+$ ions showing (a) the entire spectrum, (b) the oxygen peak, and (c) the high-energy onset of the background for a 3-MPA SAM adsorbed from the gas phase on Au(111). The spectra are normalised to the maximum background intensity of the first spectrum measured.

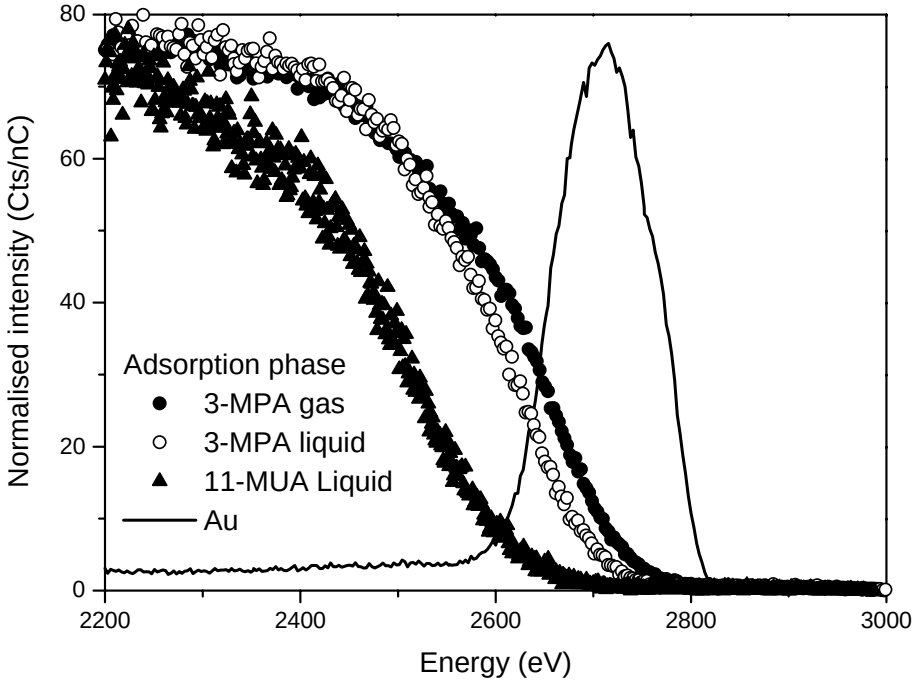
LEIS: gas *vs.* liquid phase adsorption

Surface oxygen content



Change in the oxygen peak area with increasing ion dose for 3-MPA and 11-MUA SAMs adsorbed from the gas or liquid phase on Au(111). Measurements were done with 3 keV $^4He^+$ ions. Peak areas were determined by fitting with a Gaussian after linear background subtraction.

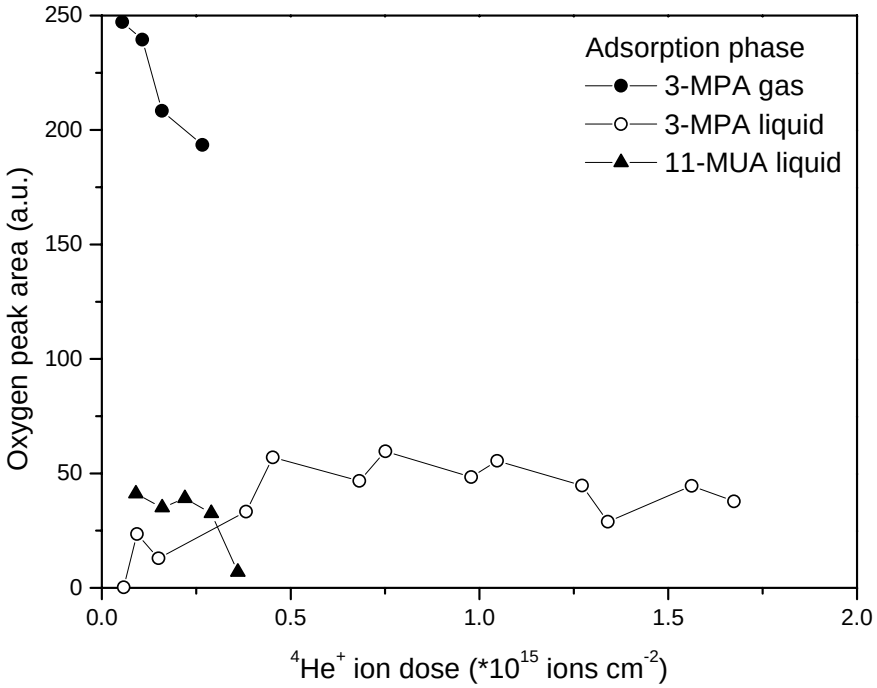
Film thickness



LEIS spectra measured with 3 keV $^4He^+$ ions showing the high-energy onset of the background for 3-MPA and 11-MUA SAMs adsorbed from the gas or liquid phase on Au(111). A spectrum from clean Au(111) is shown for comparison with the Au peak normalised to the same height as the SAM/Au spectra at 2200 eV.

LEIS: gas *vs.* liquid phase adsorption

Surface oxygen content

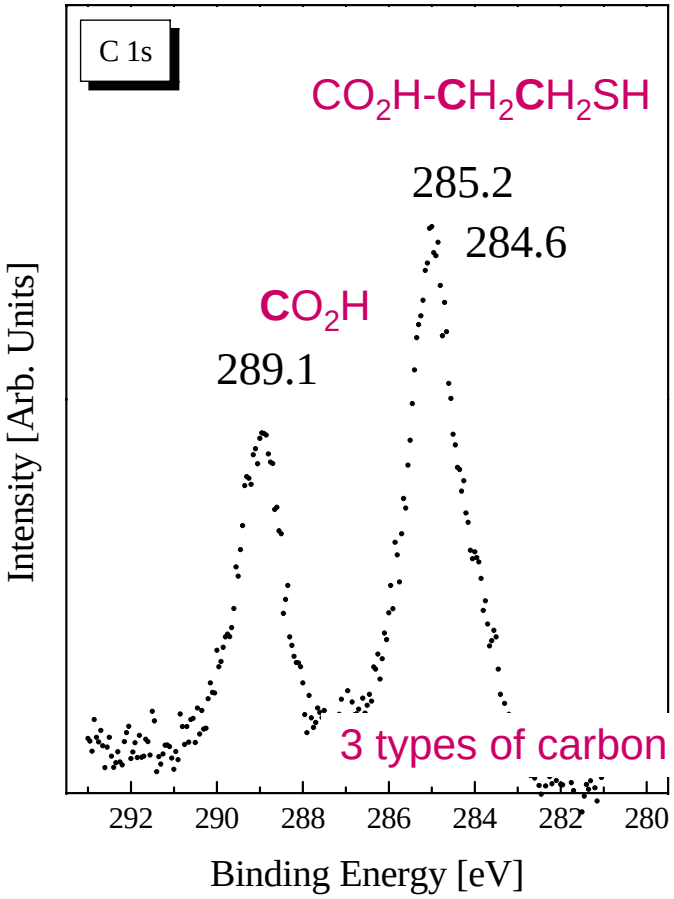


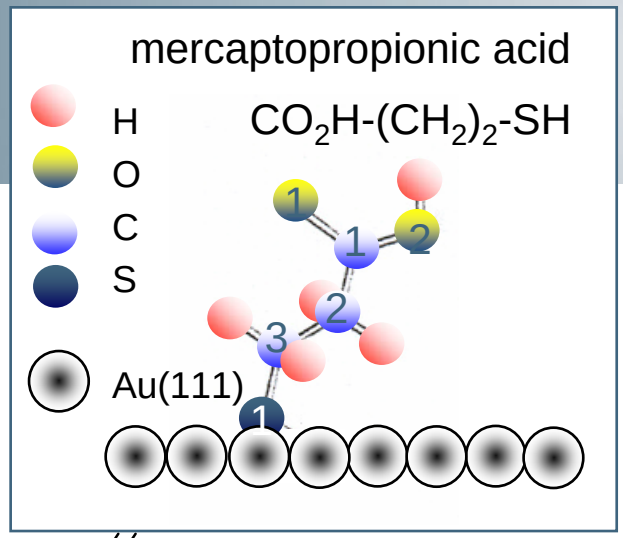
Sample	Thickness (Å)	Theoretical thickness (Å)
3-MPA(g)	4 ± 1	4.5
3-MPA(l)	6.5 ± 2	4.5
11-MUA(l)	11 ± 2	13.9

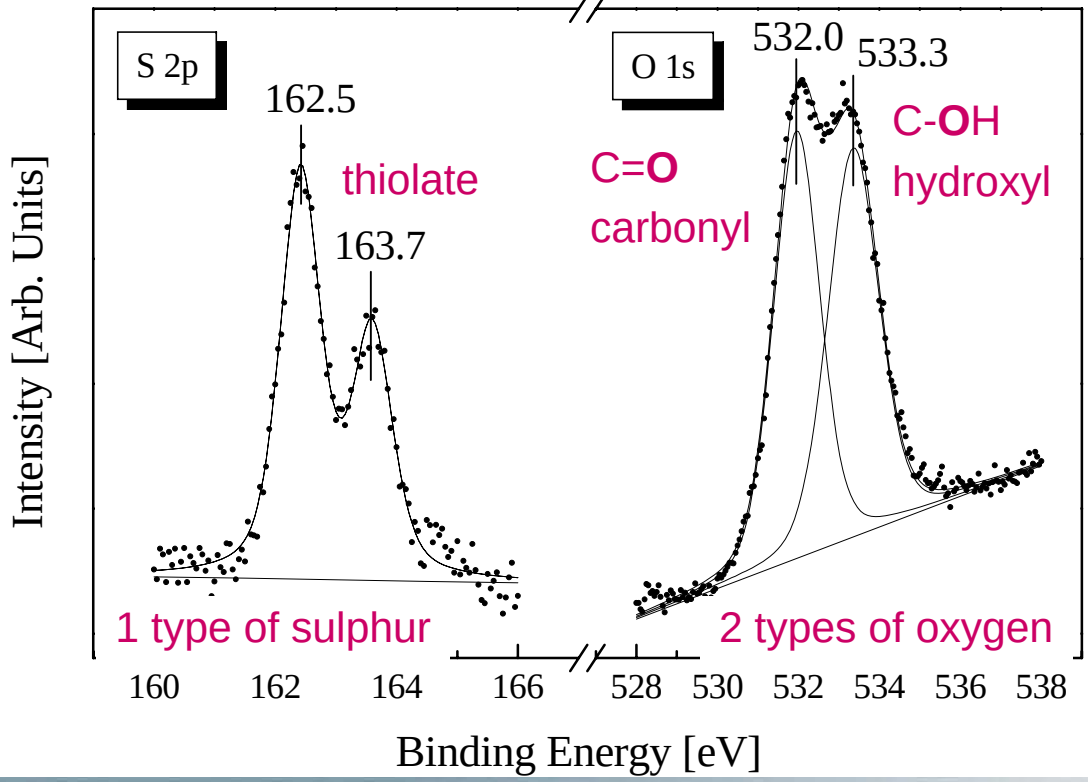
Change in the oxygen peak area with increasing ion dose for 3-MPA and 11-MUA SAMs adsorbed from the gas or liquid phase on Au(111). Measurements were done with 3 keV $^4He^+$ ions. Peak areas were determined by fitting with a Gaussian after linear background subtraction.

XPS: gas phase adsorption of 3MPA

C.M. Whelan *et al.*, Thin Solid Films (2005)



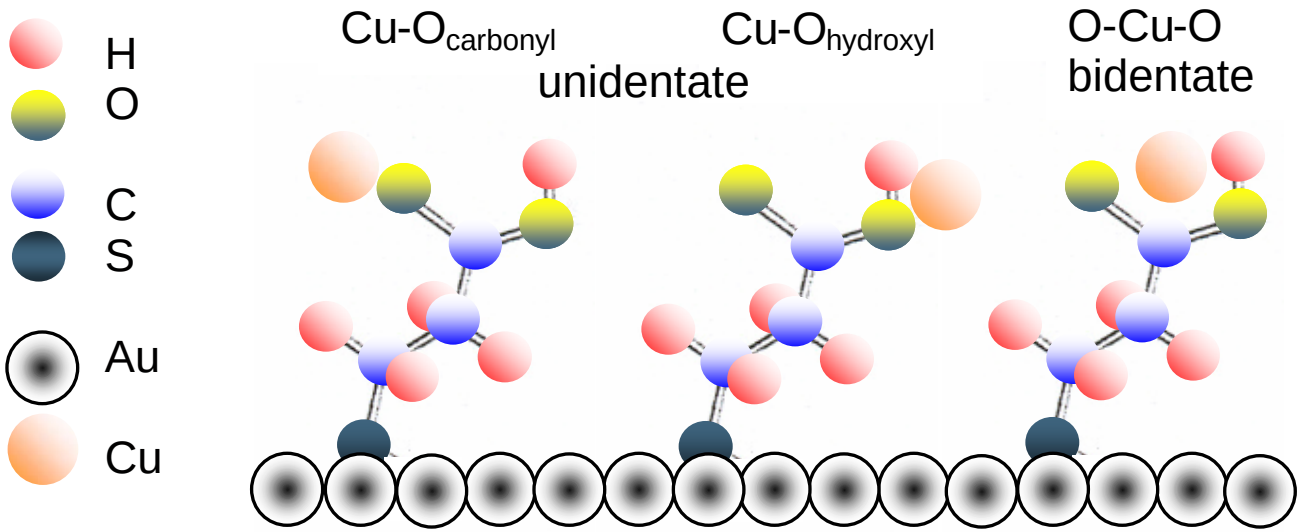




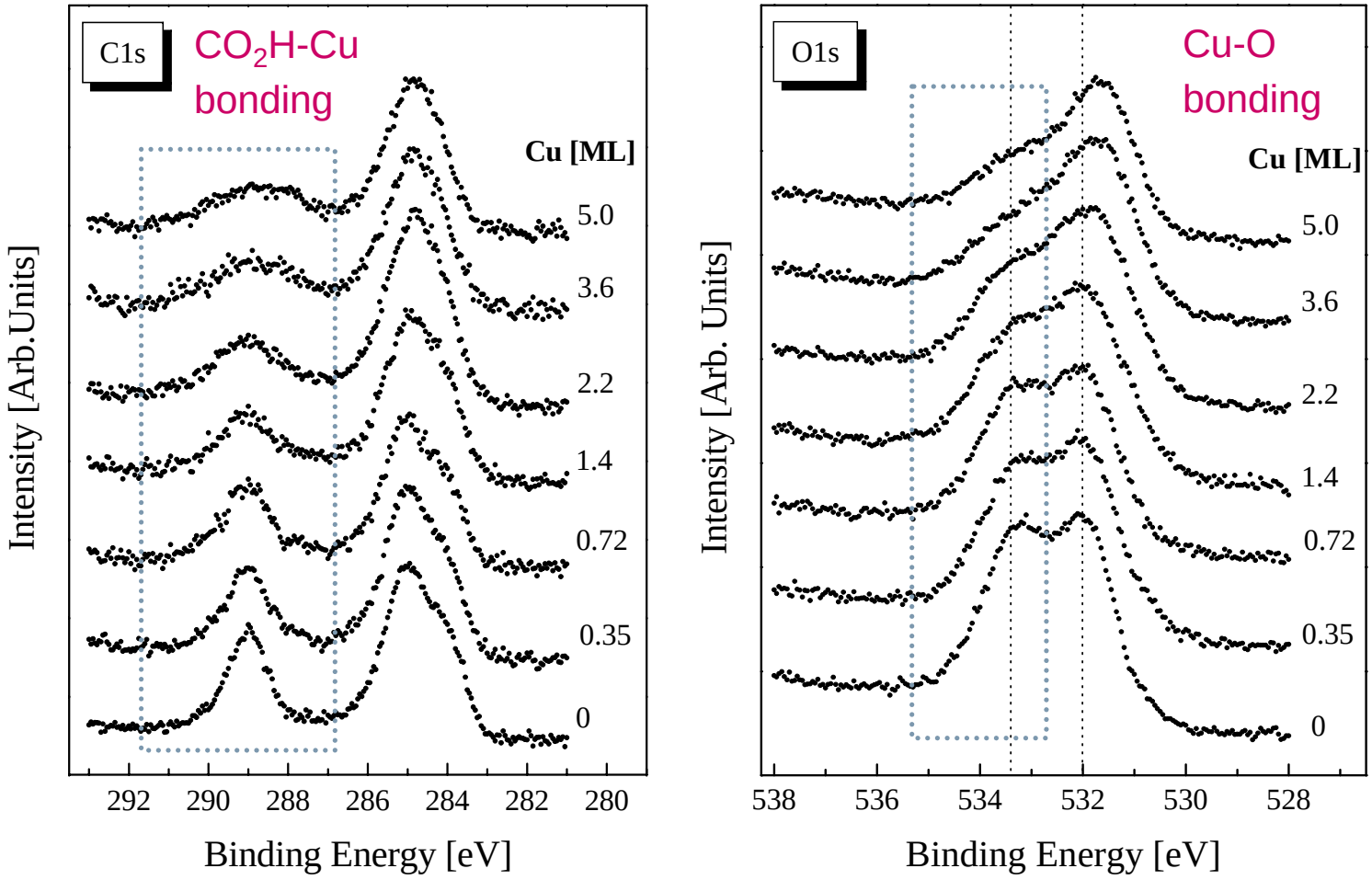
J. Ghijsen and J.-J. Pireaux

LISE, FUNDP, Namur, Belgium.

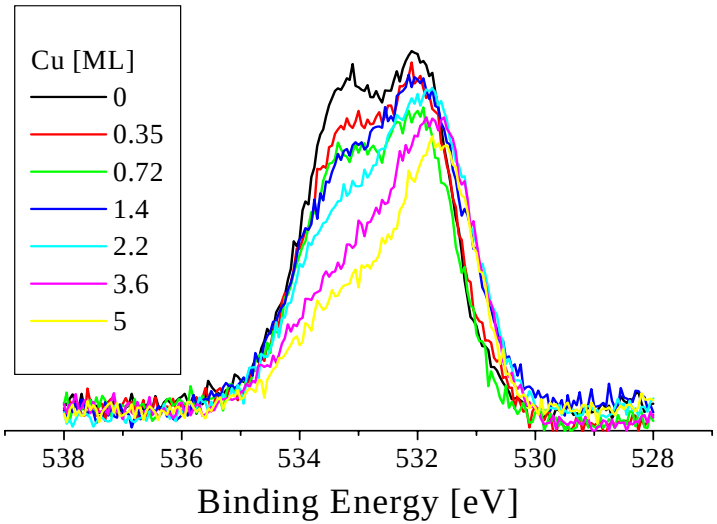
Cu/CO_2H-SAMs: possible bonding interactions

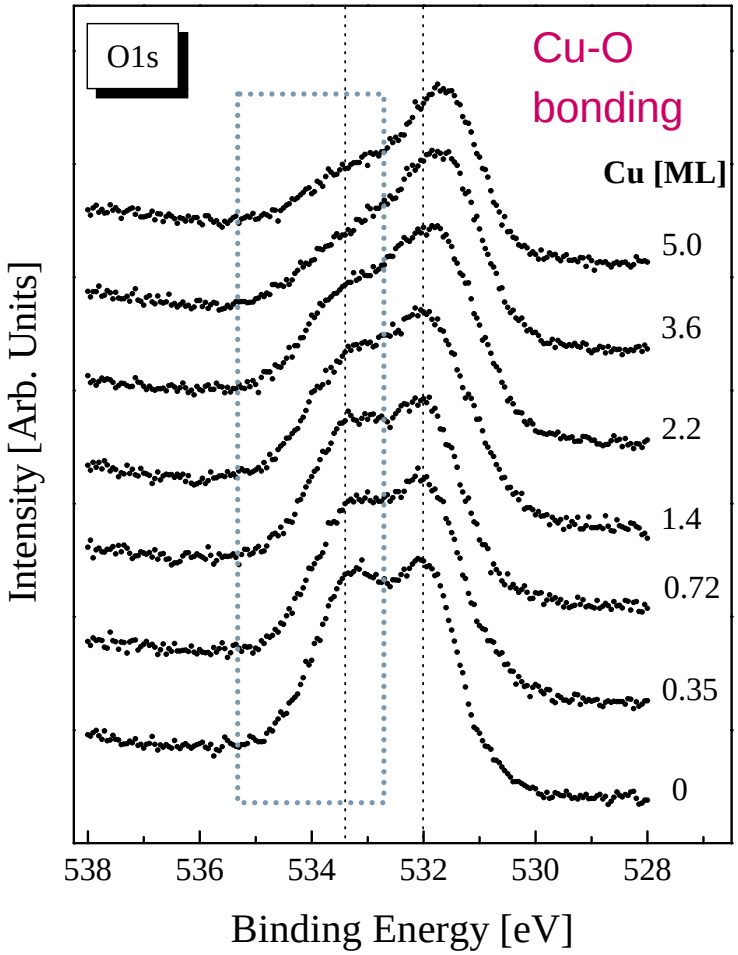


XPS: evaporation of Cu on 3MPA



XPS: evaporation of Cu on 3MPA

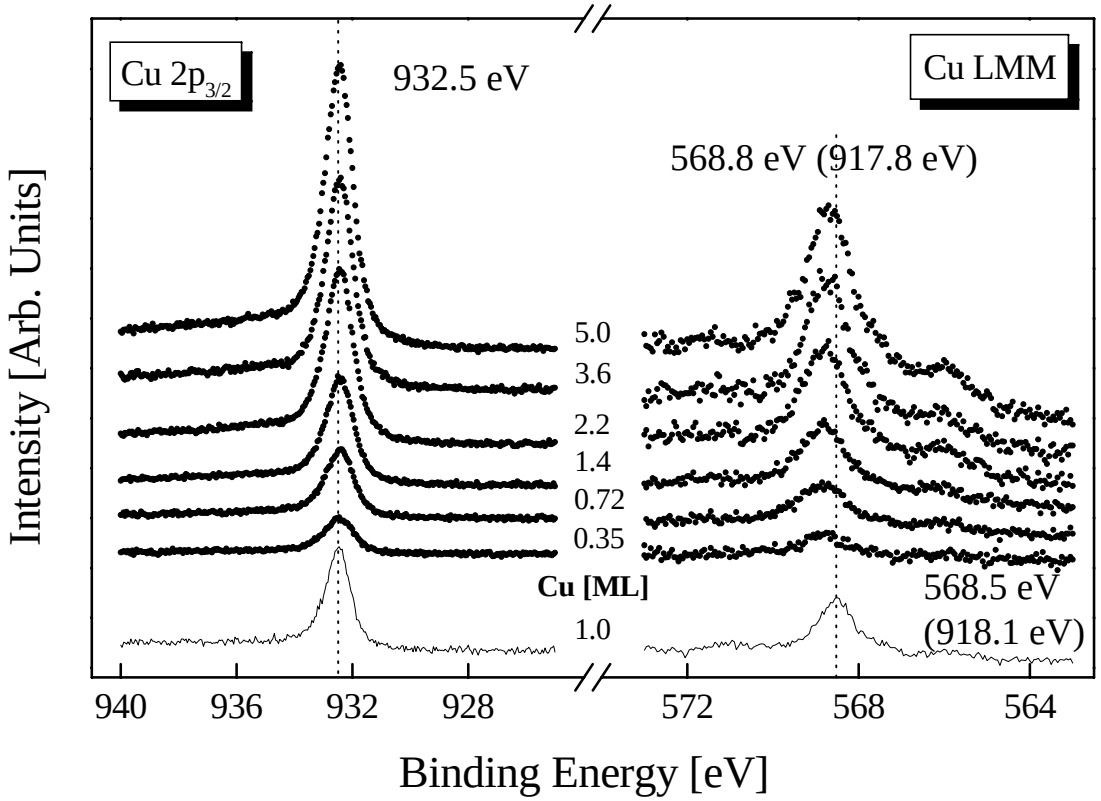


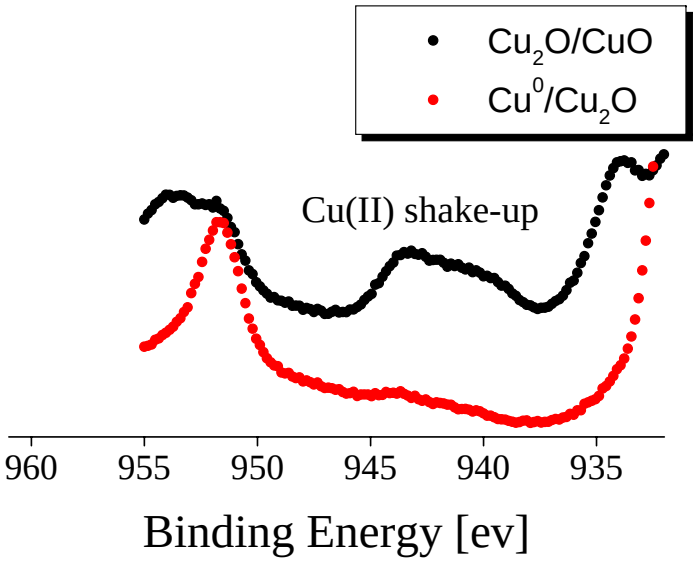


Cu interacts with **CO_2H** group

Selective deposition at **O**H site

XPS: evaporation of Cu on 3MPA





- Cu-O interaction weak and/or Cu clusters
- Cu oxidation state Cu(0)-Cu(I)
- no Cu penetration to Au surface

(3) Cu/CO_2H-SAM characterization - conclusions

- **LEIS**

  Different CO_2H-SAMs for gas *vs.* liquid phase formation :

  - Thickness 4 *vs.* 6.5 Å
  - Surface oxygen content x 5 difference

- **XPS**

  Thiolate surface intermediate with an intact carboxylic acid function

  Cu adsorption :

  - induces changes in carboxylic acid C 1s
  - preferential modification of the hydroxyl group
  - indicating unidentate complexation
  - Cu 2p comparable with bulk suggests cluster growth and weak Cu-CO_2H-SAM interactions
  - No penetration to the Au surface

Final remarks

- **ALD of WC_xN_y/various-SAMs**

Terminal group and alkyl chain length determine growth behavior

Vary substrate structure & chemistry to selectively control growth

- **SAMs as Cu diffusion barrier**

Cu silicide formation: SAM-$SiCl_3$ show enhanced inhibition attributed to high thermal stability and dense packing of SAM but no no obvious effect of chain length or terminal group

Adhesion: significant effect from head group, SAM-$Si(OCH_3)_3$ less densely packed may allow Cu penetration, XPS fracture analysis shows failure at SAM/SiO_2 interface (vs. Cu/SAM for $SiCl_3$)

SAM composition impacts adhesion & barrier properties

- **Characterization of Cu/CO_2H-SAM**

LEIS reveals SAM outer most surface

XPS identifies exact SAM-metal bonding

Acknowledgements

- F. Clemente, A.-C. Demas[$], A. Martin Hoyas, J. Schuhmacher,
- L. Carbonell, T. Conard, B. Eyckens, O. Richard, Y. Travaly, D. Vanhaeren,
- Rudy Caluwaerts, Caroline de Meurisse, and IMEC P-line.
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THANK YOU !

[$]CEA/DRT/LETI/DPTS/SCPIO/LCPO, Grenoble, France.