3.1.2 Metal Nitride CVD - Conductive Diffusion Barriers

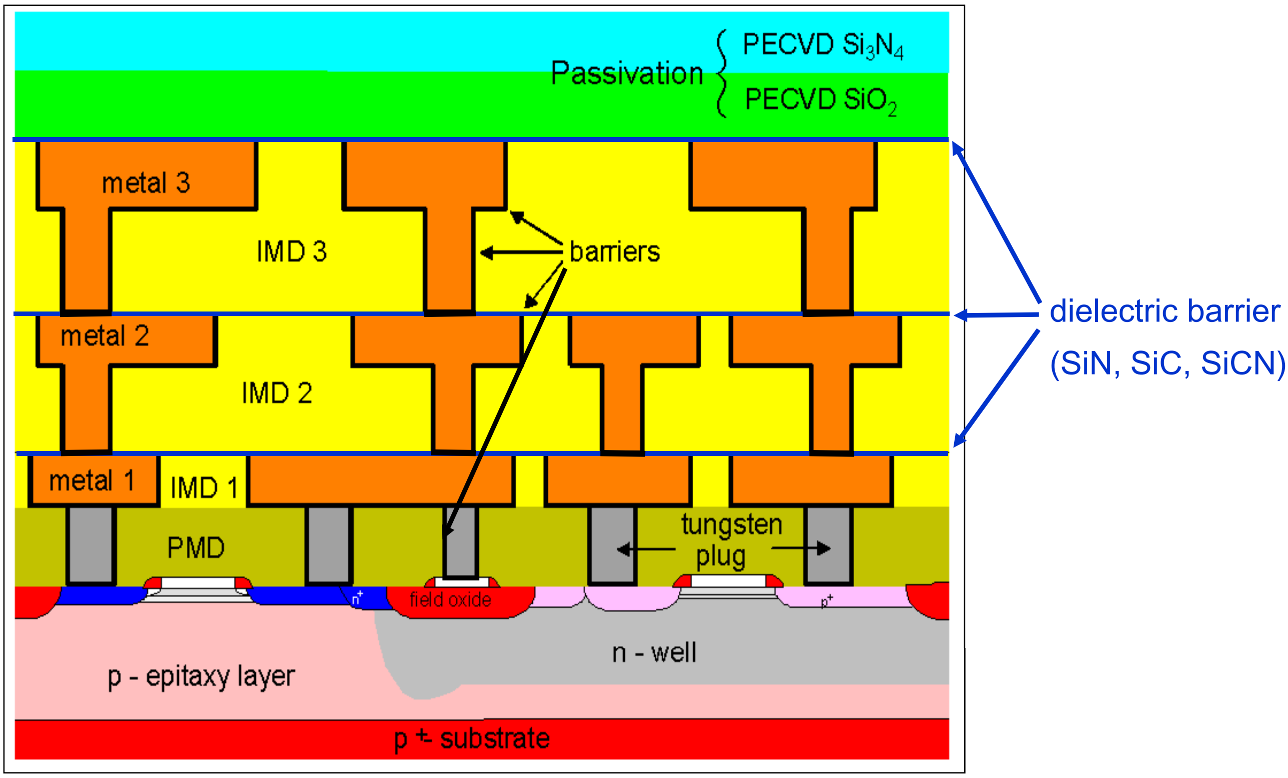
- Introduction – Challenges
- Comparison of diffusion barrier deposition techniques – status
- Metal and metal nitride CVD precursors
- CVD of TiN
- CVD of WN

Application of (transistion) metal nitride films:

- ➢ Gate electrode – work function adjustment
- ➢ Barrier/liner for W-CVD
- ➢ Barrier/liner for Cu damascene interconnects (may also act as CMP stop layer depending on material)

Status: 01.04.2014

Thin CVD films in copper Damascene metallization

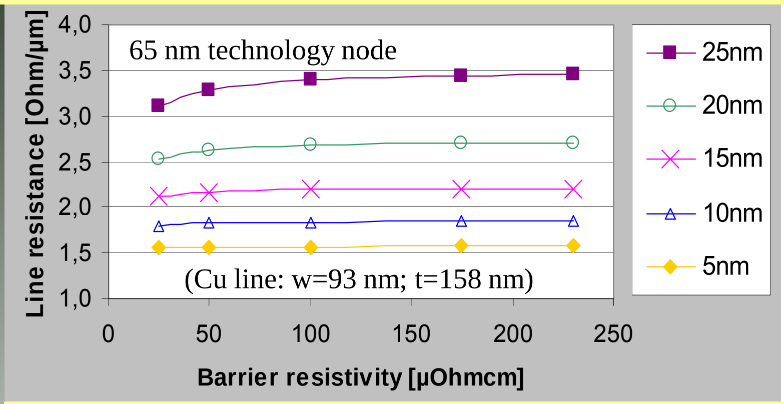


Conducting barriers (PVD, CVD, ALD): (Ta, TaN/Ta, TiN, WN)

- Diffusion barrier against Cu diffusion and drift
- Liner for Cu deposition (adhesion, low interface diffusion – EM)
- CMP stop for Cu CMP

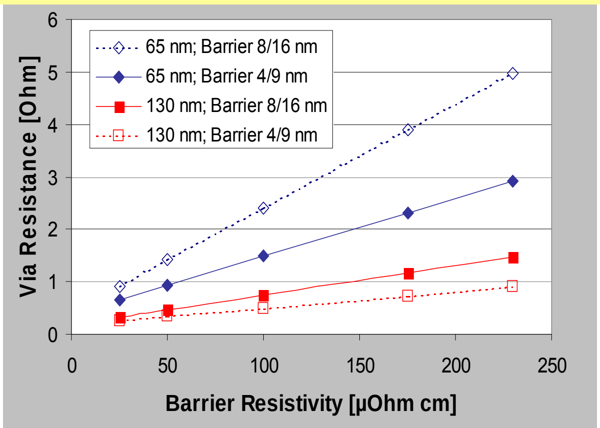
Barrier resistivity and thickness impact on via and line resistance

Line resistance: impact of barrier resistivity and thickness



- Impact of barrier thickness significant
- 1/5 of barrier thickness → decreases line resistance by half
- Thickness impact increases with further scaling (not shown here)
- Resistivity of barrier negligible

Via resistance: impact of barrier resistivity



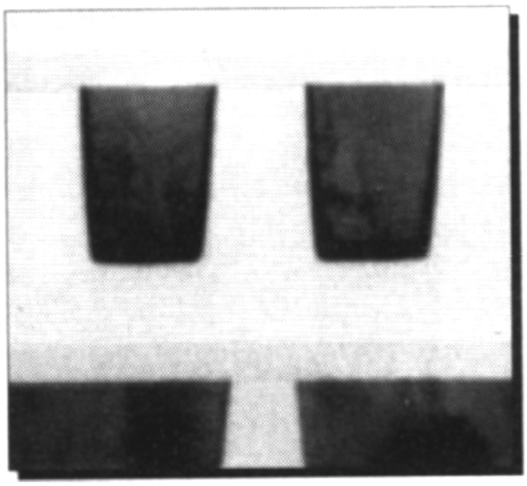
- Impact of barrier resistivity and thickness significant for both technology nodes
- Impact increases with further scaling

Node	via diameter	via height	barrier thickness side	barrier thickness bottom
130	170	255	8	16
65	93	135	4	9

Requirements for conducting CVD barriers in copper interconnects

Diffusion Barriers:

- Ultrathin, but nevertheless very stable
    - High density / no or stuffed diffusion paths
    - Low defect level
    - Thermodynamically stable
- Good adhesion to underground and Cu
- Low stress
- Low resistivity:
  e.g. < (1000… 300) µΩcm
- Conformal (may cause CMP re-work: if stop on barrier is used)



1. 1. SEM image of copper interconnects on Intel's 90 nm process generation. The liner film consumes ~15% of the interconnect cross-sectional area. (Source: Intel)

Deposition techniques for barriers

PVD	CVD	ALD	Electroless
Physical vapour deposition	Chemical vapour deposition	Atomic layer deposition	Catalytic plating
• Industrial standard: Ta and TaN for Cu metallization	• Industrial standard: TiN (e.g. for W-CVD)	• Research focus: different materials (TiN, WCN; TaN and others)	• Use as cap layer: CoWP for better interface Cu/cap electromigration ↑ lifetime
Advantages			
• Low deposition T • Good control of barrier composition	• Good process control • High step coverage	• Potential of 100% step coverage • Very thin closed layers	• Selective • Self aligned → no texturing step
Disadvantages			
• Low step coverage	• Partly high deposition T • Partly use of toxic reactants • Risk of particle formation using NH_3	• Nucleation strongly depends on surface state	• Cleaning step of the Cu and ILD surface • Activation step of Cu surface to improve catalytic nature

Precursors for barrier CVD

Precursors

Metal organic compounds	Halide chemistry
• Carbonyls, alkenes, alkynes, arenes, cyclopentadienyls, β-diketonates ….	• MeF_x, $MeCl_x$, $MeBr_x$ MeI_x
• Big diversity of compounds and properties • Big effort in design of new precursors	• Available commercially
• Often not available commercially • High C and O contaminations in the film • Vapour pressure of at least 13 Pa essential → for a sufficiently high deposition rate → excludes many potential precursors because thermal decomposition before reaching a sufficiently high vapour pressure	• Mostly solids → low volatility • Generally no thermal decomposition below 500°C • Halogen-contaminated films • Corrosive products → e.g. HF (addition of reducing agents H_2 or SiH_4) • Toxic

Titanium nitride CVD

- Application and integration aspects
- Precursors and reactions
- Example:

  MOCVD of TiN using TDMAT precursor

TiN CVD: Application and integration aspects

TiN: A multi functional material in semiconductor industry

Deposition techniques: PVD (reactive sputtering), ALD and CVD
(Variety of processes commercially available for different applications)

Fields of application:

- Improving electromigration performance of Al interconnects as base and cap layer
- Glue layer / liner for metal deposition (e.g. for W on dielectric = adhesion promoter)
- Lithography: Anti reflective coating (ARC)
  Hard mask (HM) material in adv. patterning schemes
- Barrier layer to prevent undesired material interactions, e.g. between:
  - Cu and dielectrics: on-chip interconnects and through silicon vias (TSVs)
  - WF_6 or HF in W-CVD and other materials (Si, Ti silicide, Al) - protect contact from aggressive fluorine chemistry during W-CVD
- High aspect ratio contacts, combination of $TiSi_2$ and TiN liner for tungsten plugs – CVD: use of $TiCl_4$ precursor
- Metallization of Ta_2O_5-capacitors (DRAM) – CVD: use of $TiCl_4$ or metal organic precursor
- Barrier layer in Cu or Al metallization schemes, favourable for damascene architectures – CVD: use of metal organic precursors TDMAT or TDEAT

TiN CVD: Application and integration aspects

Why CVD ?

Good step coverage in case of high aspect ratios (W contacts, vias)

→ Important for ultra thin barrier films in high aspect ratio patterns

Technical requirements for use:

- State of the art single wafer cluster tool with CVD-chamber (e.g. Applied Materials P 5000 with TxZ™-chamber, Novellus PRISM™)
- Delivery system for liquid precursor
  - bubbler or liquid inject for TDMAT and TDEAT
  - vapour MFC for $TiCl_4$

Thermal budget:

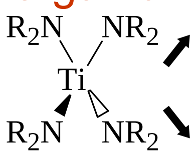
- $TiCl_4$: < 5 min & 550°C ... 630°C
- MOCVD: < 5 min & 300°C ... 400°C

TiN CVD: Precursors and reactions

inorganic

$TiCl_4 + NH_3 + {}^1/_2\, H_2 \xrightarrow{\text{reduction of metal halide}} TiN + 4HCl$ reaction I

organic



$+ NH_3 \xrightarrow{\textit{transaminiation}} TiN + 4HNR_2$ reaction II

$\xrightarrow{\textit{pyrolytic decomposition}} TiN + \text{amines} + TiC + \ldots$ reaction III

R ... alkyl group

R = CH_3 tetrakis dimethyl amino titanium; is the favourite for reaction III

R = C_2H_5 tetrakis diethyl amino titanium; is the favourite for reaction II

R determines vapour pressure and reactivity of the precursor

Processes commercially available for all of the three reactions (e.g. Novellus, AMAT)

additional organic precursors

$Ti(OC_2H_5)_4$, $Ti(Bu^tN{=}CHCH{=}NBu^t)_2$, $Ti(acetylacetonat)_3$

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TiN CVD: Precursors and reactions

Comparison of $TiCl_4$ and TDMAT process

	$TiCl_4$	TDMAT
Precursor		
vapour pressure precursor delivery commercially available	40 Torr @ 50°C vapour MFC yes	0.6 Torr @ 50°C bubbler, direct liquid inject yes
Process characteristics		
temperature range additional source gases byproducts particle behaviour application of plasma	500°C ... 800°C NH_3, H_2 corrosive NH_4Cl salt formation to reduce Cl at lower deposition temperatures	350°C ... 400°C Ar, N_2 or He as carrier gas non corrosive, toxic amins o.k. as post deposition treatment to reduce impurities
Film properties		
resistivity (lowest reported values) conformality impurity	100 µΩcm with plasma treatment near 100% chlorine, hydrogen	170 µΩcm with plasma treatment near 100% carbon, hydrogen; oxygen uptake if exposed to air

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CVD of Copper diffusion barriers: TiN by CVD

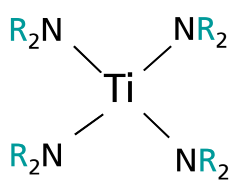
Ti based barrier

- inorganic route: $TiCl_4 + NH_3$ → T>600°C, and formation of HCl
- metalorganic route:

TDMAT

R = CH_3

- higher vapour pressure
- more reactive



R → affects vapour pressure and reactivity

TDEAT

R = $_2HC-CH_2$

- lower vapour pressure
- less reactive

Pyrolysis

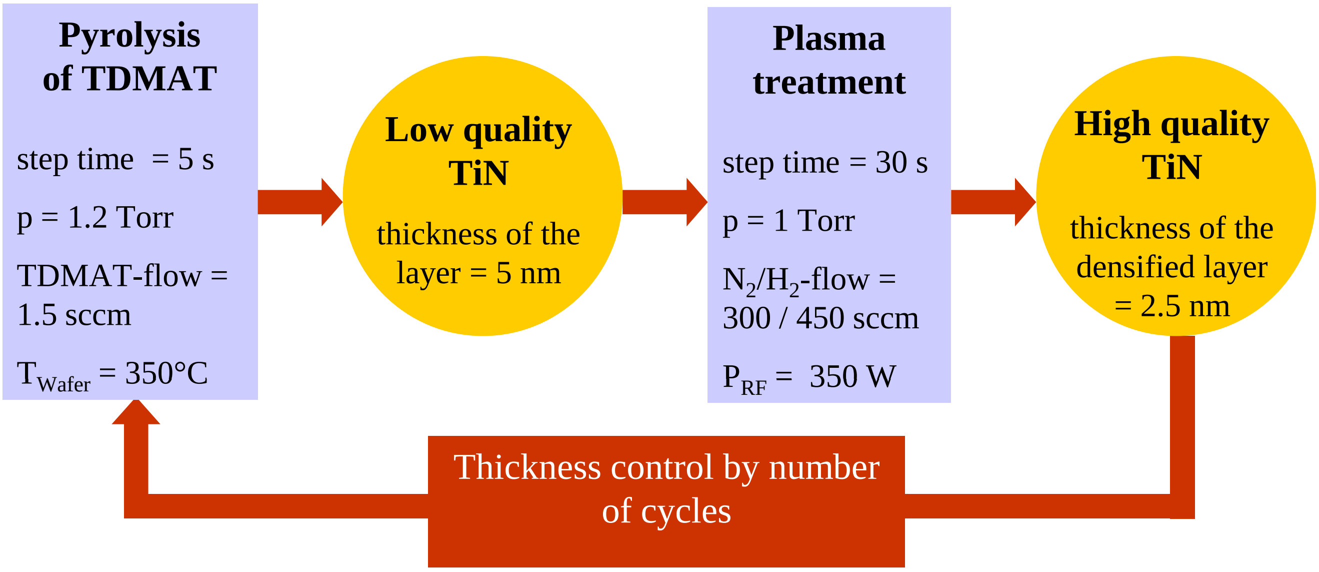
favoured reaction

reaction with NH_3 or plasma activated with H_2/N_2

- lower contamination level
- higher step coverage

Multistep process for high quality TiN

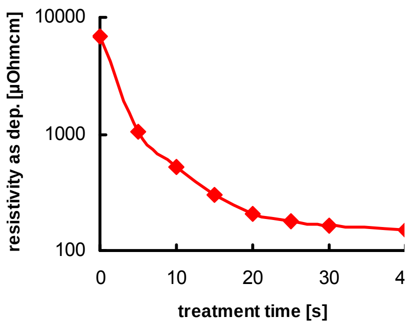
Method was introduced by
M. Danek and coworkers (Applied Materials), 1995

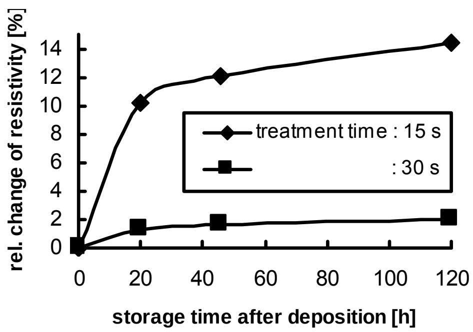


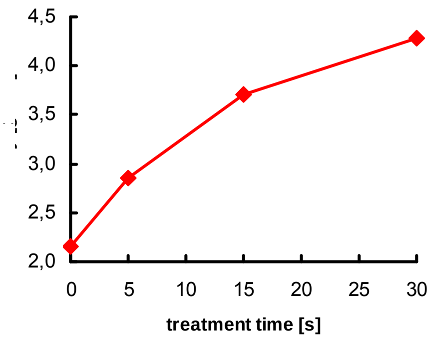
CVD of Copper diffusion barriers: TiN by CVD

Deposition process with TDMAT

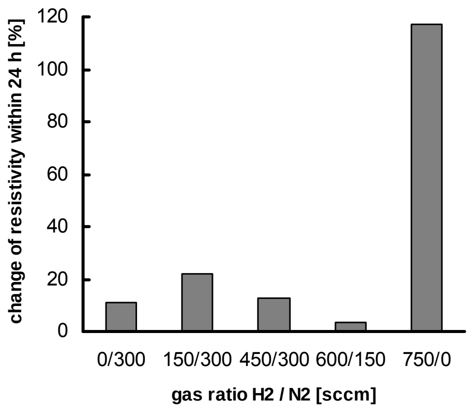
- plasma parameters determine the film properties → resistivity and its change within 24 h







- long plasma treatment → higher stability
  - → higher density
  - → lower resistivity
  - → lower impurity level
- drawback: plasma treatment 6 times longer than deposition step
- H_2/N_2 plasma → replacement of C → volatile CH_4
  N_2 essential for a stable film → introduction of additional N



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CVD of Copper diffusion barriers: TiN by MOCVD from TDMAT

Film properties

	without plasma treatment	multi step process with plasma treatment
Spec. el. resistivity	≈ 8000 µΩcm	170 µΩcm
Stability of resistivity if exposed to air	increase ≈ 200%	increase < 2%
Density (bulk value = 5.2 g/cm³)	2.2 g/cm³	4.8 g/cm³
Film stress (all compressive)	- 300 MPa (as dep.) - 500 MPa (after air exp.)	- 1400 MPa (as dep.), no change after air exp.
Microstructure	amorphous like	polycrystalline
Impurities	≈ 25 at.% C, ≈ 25 at.% O if exposed to air	6 at.% C, 5 at.% O if exposed to air
Barrier stability against copper diffusion (electrically tested with pn-diodes)	fails already at 350°C	stable up to 450°C

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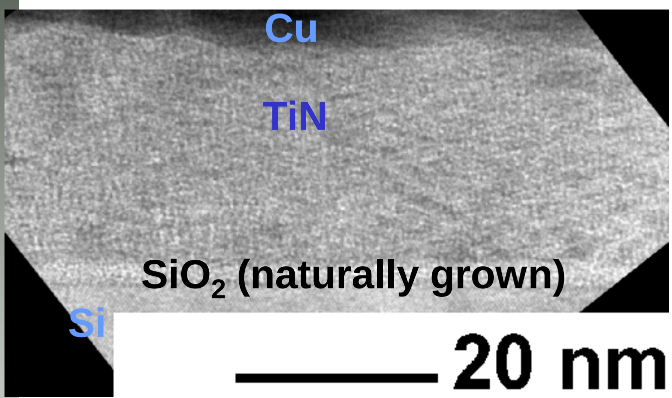
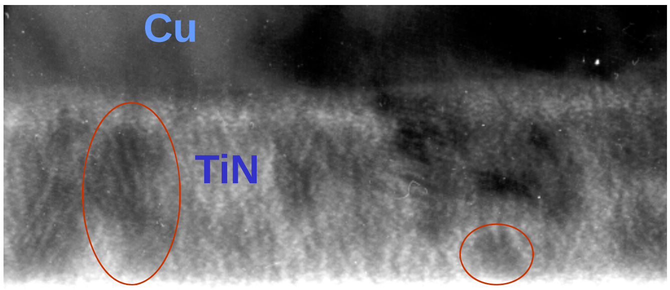
TiN-CVD: Example MOCVD of TiN using TDMAT precursor

Micro structure of MOCVD TiN

without plasma treatment



multi step process with plasma treatment



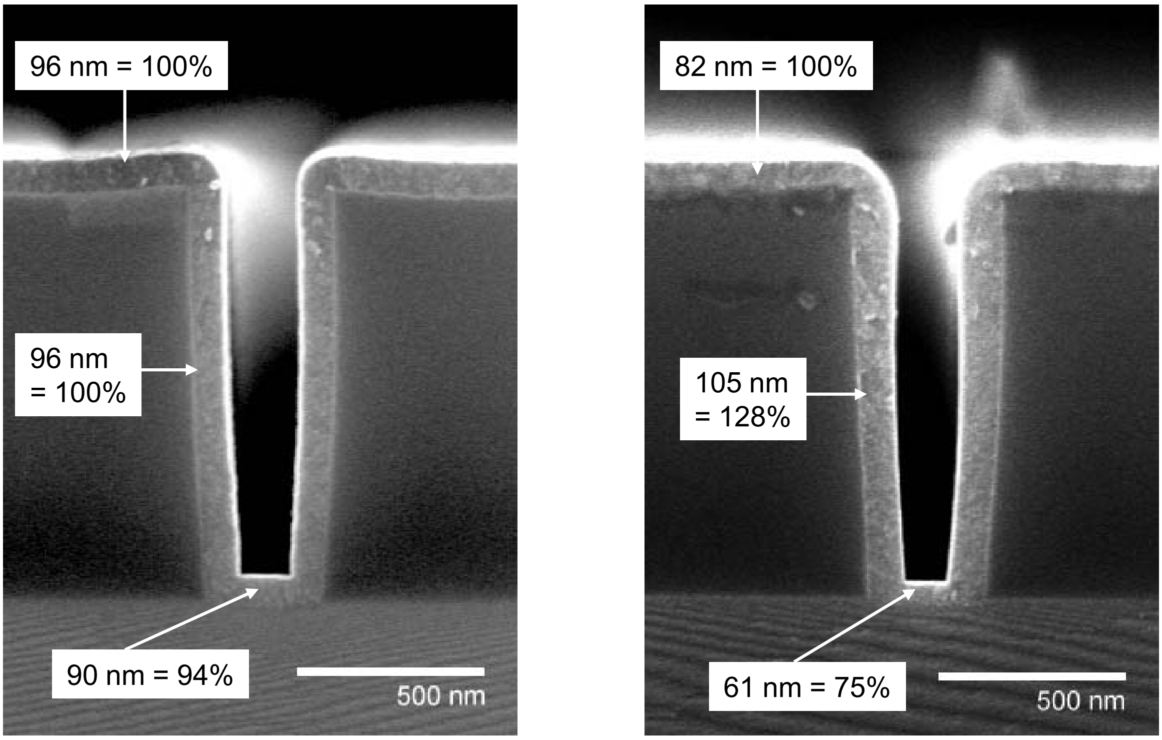
- XRD amorphous
- small regions (3 nm) with ordered structure visible in high resolution TEM, embedded in amorphous material

- polycrystalline (one get (111) and (200) TiN peak in XRD)
- wide grain size distribution
  - ***grains reaching through the entire film***
  - ***small grains***

Step coverage

CVD-TiN in a 0.3 µm oxide trench with an aspect of ration 3.5

Without plasma treatment | **Multi step process with plasma treatment**



W based Barriers

WF_6 → Gas at room temperature with high vapour pressure of 133 kPa @25°C

- Also use of WCl_6 (solid)
- Metalorganic W precursors mostly solid

WN_x Deposition

- Thermal CVD with WF_6 and NH_3 → salt formation NH_4F
- Thermal CVD with metalorganic precursor → high deposition temperature > 500°C
- PECVD with $WF_6/NH_3/H_2$ → salt formation NH_4F, reduced step coverage
- PECVD with $WF_6/N_2/H_2$ → low deposition temperatures, reduced step coverage, amorphous or crystalline films

CVD of Copper diffusion barriers: WN by PECVD

PECVD process for amorphous ultrathin WN_x films

PRECISION 5000™ configuration

Chemistry: WF_6(Ar)/N_2/H_2

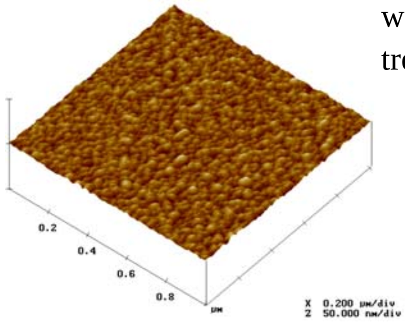
Steps of the process

H_2 + N_2 plasma treatment of substrate before deposition step
uniform smooth film

Deposition parameters:

- T = 380-400°C
- rf power = 50 W
- H_2/WF_6 = 50-80
- N_2/WF_6 = 80-110
- p = 340-430 Pa

H_2 plasma treatment of the film after deposition
reduction of F level

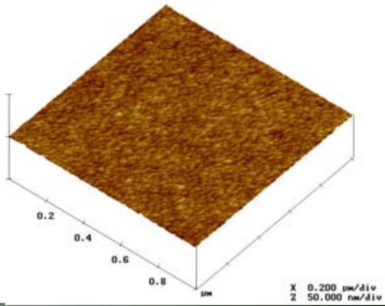


without H_2+N_2 plasma treatment of SiO_2 surface

RMS:	0.86 nm
R_a:	0.652 nm
R_{max}:	4.818 nm

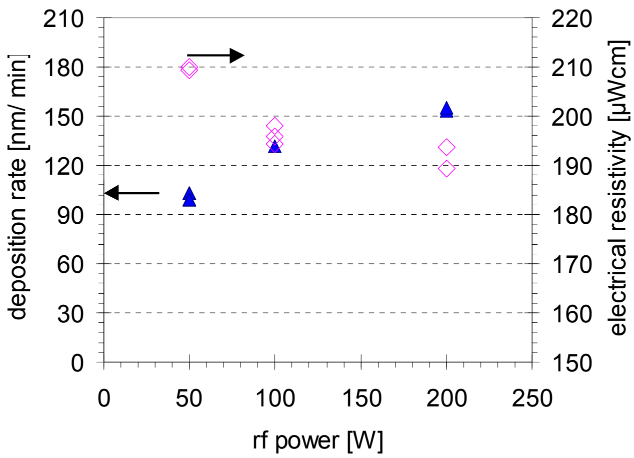
with H_2+N_2 plasma

RMS:	0.378 nm
R_a:	0.296 nm
R_{max}:	1.945 nm



CVD of Copper diffusion barriers: WN by PECVD

Influence of process conditions on the deposition rate



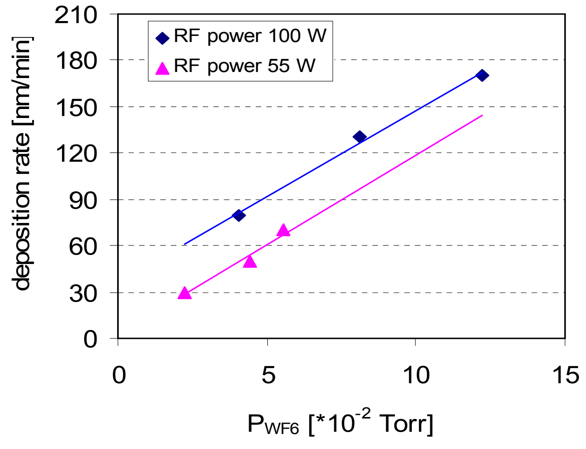
RF power

- Deposition mainly driven by plasma
- Decrease of deposition rate by 50 % between 200 - 50 W
- Slight increase of electrical resistivity

→ low RF power for low deposition rates

WF_6 partial pressure

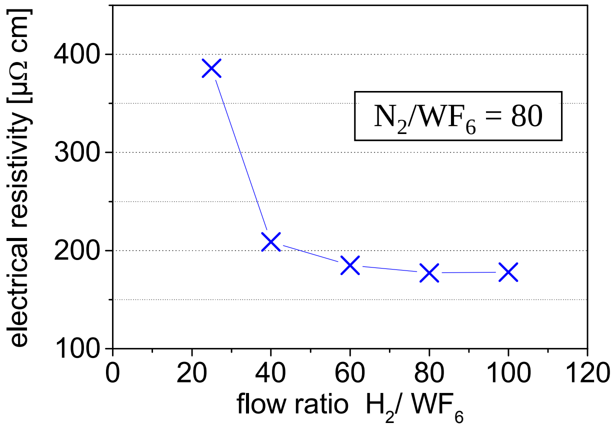
- Low p_{WF6} results in low deposition rate
- Low p_{WF6} with rf power of 55 W leads to further decrease of the deposition rate

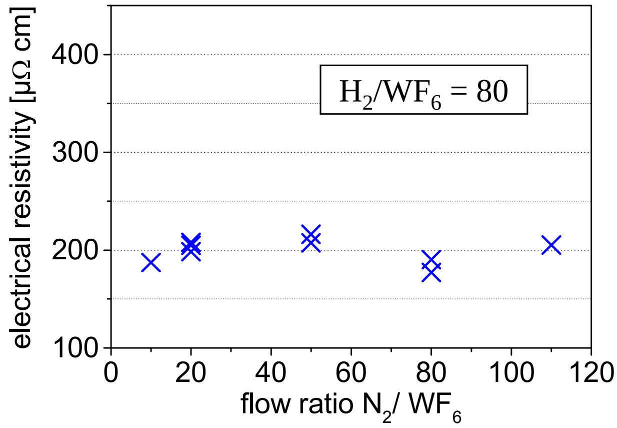


(T = 400°C, p = 670 Pa, p_{H2} = 530 Pa, p_{N2} = 125 Pa)

CVD of Copper diffusion barriers: WN by PECVD

Influence of the Gas Mixture on the Electrical Resistivity



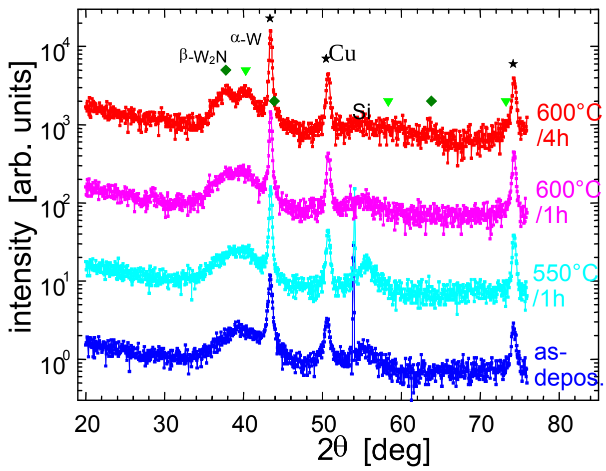


- Extreme nitrogen and hydrogen content within the gas mixture moderately influences the electrical resistivity
- Low gas flow ratios for H_2/WF_6 → higher resistivity
  no effective removal of fluorine

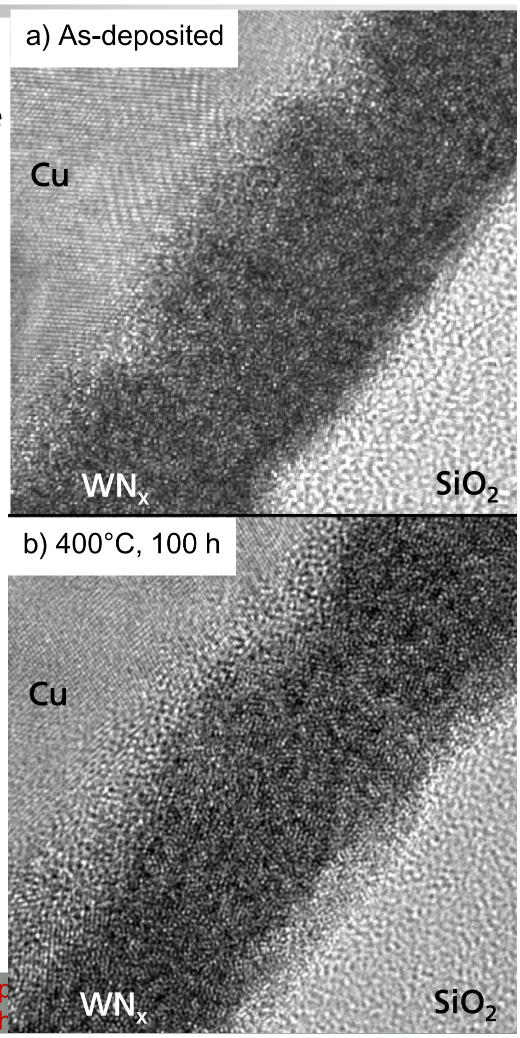
CVD of Copper diffusion barriers: WN by PECVD

Microstructural investigations

- Amorphous microstructure in the as-deposited state
- Remain of amorphous microstructure after heat treatment in vacuum at 400°C/100h
- Composition of WN_x: x=0.25 → $W_{80}N_{20}$
- Commencing crystallization at 600°C/1h in vacuum and progressive with longer exposure time
  → high amorphous amount



GI-XRD of Si/100 nm SiO_2/10 nm $W_{80}N_{20}$/ 50 nm Cu

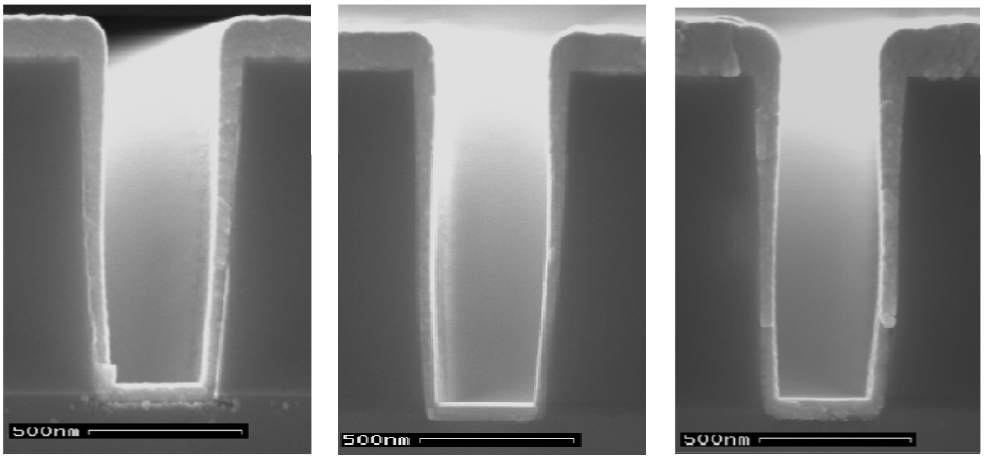


CVD of Copper diffusion barriers: WN by PECVD

Impact of spacing on step coverage: WN_x in 0.4 µm wide trenches (AR ~ 2.5) after deposition at *different spacings between shower head and wafer surface*

250 mils | 400 mils | 600 mils

PRECISION 5000™ (Lamp heated WCVD chamber)

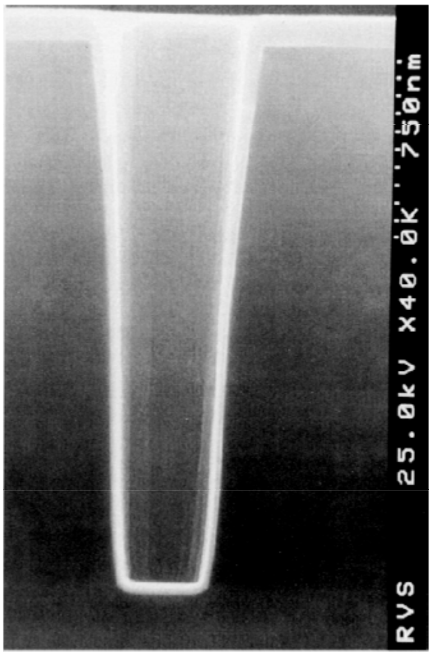


	film thickness [nm]	conformality [%]	film thickness [nm]	conformality [%]	film thickness [nm]	conformality [%]
top	138	**100**	128	**100**	181	**100**
wall at the half trench height	59	**43**	45	**36**	54	**30**
wall near the bottom	50	**36**	36	**28**	45	**25**
bottom	67	**49**	53	**42**	67	**37**

K. Richter et al. (TU Chemnitz), AMC 2000, MRS Conf. Proc. ULSI XVI, MRS Warrendale, PA, 2001, p. 301-306.

CVD of Copper diffusion barriers: WN by PECVD

SEM of a contact structure with 0.35 µm opening and 5:1 aspect ratio



⇒ up to 60 % step coverage at optimal process conditions

- **Applied Materials Centura™ WxZ chamber**
- **reactive gases: WF_6, N_2, H_2 and Ar as diluent**

Source: Kevin K. Lai (Applied Materials) et al., Thin Solid Films, 332 (1998) 329-334