

CVD Reactor



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Precursor Volatility



Aluminum 2.27 μΩcm, easily etched, Al dissolves in Si, GaAs + Al → AlAs + Ga Gas diffusion barriers, Al on polypropylene, food packaging = chip bags, party balloons, high optical reflectivity



Al deposits selectively on Al surfaces, not on SiO₂ Laser-induced nucleation 248 nm only surface adsorbates pyrolysed 193 nm gas phase reactions, loss of spatial selectivity control

TMA

large carbon incorporation, Al₄C₃, RF plasma, laser

 $Al_2(CH_3)_6 \longrightarrow 1/2 Al_4C_3 + 9/2 CH_4$ under N₂

 $Al_2(CH_3)_6 + 3H_2 \longrightarrow 2Al + 6CH_4$ under H_2

TMAA



 $(CH_3)_3N-AlH_3 \longrightarrow Al + (CH_3)_3N + 3/2 H_2$ below 100 °C



 $(CH_3)_3N-AlH_3 \longrightarrow Al + (CH_3)_3N + 3/2 H_2$ below 100 °C

Aluminoboranes



at 280 °C, low carbon incorporation

Tungsten

5.6 $\mu\Omega$ cm, a high resistance to electromigration, the highest mp of all metals 3410 °C.

$$2 \operatorname{WF}_6 + 3 \operatorname{Si} \rightarrow 2 \operatorname{W} + 3 \operatorname{SiF}_4$$

 $WF_6 + 3H_2 \rightarrow W + 6HF$

 $WF_6 + 3/2 SiH_4 \rightarrow W + 3 H_2 + 3/2 SiF_4$

 $W(CO)_6 \rightarrow W + 6 CO$

Diketonate Ligands





R ₁	R ₂	Name	Abbreviation
CH3	CH3	Pentane-2,4-dionate (acetylacetonate)	acac
CH3	CF_3	1,1,1-trifluoropentane-2,4-dionate (trifluoroacetylacetonate)	tfac
CF3	CF_3	1,1,1,5,5,5-hexafluoropentane-2,4-dionate (hexafluoroacetylacetonate)	hfac
CH3	C(CH ₃) ₃	1,1-dimethylhexane-3,5-dionate	dhd
C(CH ₃) ₃	C(CH ₃) ₃	2,2,6,6-tetramethylheptane-3,5-dionate	thd
CH3	CH ₂ CH(CH ₃) ₂	6-methylheptane-2,4-dionate	mhd
C(CH ₃) ₃	CH ₂ CH(CH ₃) ₂	2,2,7-trimethyloctane-3,5-dionate	tmod
C ₆ H ₅	C_6H_5	1,3-diphenylpropane-1,3-dionate (dibenyzoylmethanate)	dbm

Diketonate Precursors



Mononuclear



Polynuclear

Copper(II) hexafluoroacetylacetonate

excellent volatility (a vapor pressure of 0.06 Torr at r. t.), low decomposition temperature, stability in air, low toxicity, commercial availability

deposition on metal surfaces (Cu, Ag, Ta) the first step, which can already occur at -150 °C, a dissociation of the precursor molecules on the surface (Scheme I).

An electron transfer from a metal substrate to the single occupied HOMO which has an anti-bonding character with respect to copper d_{xy} and oxygen p orbitals weakens the Cu-O bonds and facilitates their fission.





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SEM of Cu film, coarse grain, high resistivity



Growth rate of Cu films deposited from Cu(hfacac)₂ with 10 torr of H₂



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Cu(I) precursors

Disproportionation to Cu(0) and Cu(II)

 $2 Cu(diketonate)L_n \rightarrow Cu + Cu(diketonate)_2 + n L$



Diamond films

activating gas-phase carbon-containing precursor molecules:

•thermal (e.g. hot filament)

•plasma (D.C., R.F., or microwave)

•combustion flame (oxyacetylene or plasma torches)





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Experimental conditions:

temperature 1000-1400 K

the precursor gas diluted in an excess of hydrogen (typical CH₄ mixing ratio ~1-2vol%)

Deposited films are polycrystalline

Film quality:

•the ratio of sp³ (diamond) to sp²-bonded (graphite) carbon

•the composition (e.g. C-C versus C-H bond content)

the crystallinity

Combustion methods: high rates (100-1000 µm/hr), small, localised areas, poor quality films. Hot filament and plasma methods: slower growth rates (0.1-10 µm/hr), high quality films.

Hydrogen atoms generated by activation (thermally or via electron bombardment) H-atoms play a number of crucial roles in the CVD process:

H abstraction reactions with hydrocarbons, highly reactive radicals: CH₃ (stable hydrocarbon molecules do not react to cause diamond growth) radicals diffuse to the substrate surface and form C-C bonds to propagate the diamond lattice.

H-atoms terminate the 'dangling' carbon bonds on the growing diamond surface, prevent cross-linking and reconstructing to a graphite-like surface.

Atomic hydrogen etches both diamond and graphite but, under typical CVD conditions, the rate of diamond growth exceeds its etch rate whilst for graphite the converse is true. This is the basis for the preferential deposition of diamond rather than graphite.

Diamond initially nucleates as individual microcrystals, which then grow larger until they coalesce into a continuous film



Enhanced nucleation by ion bombardment:

damage the surface - more nucleation sites

implant ions into the lattice

form a carbide interlayer - glue, promotes diamond growth, aids adhesion

Substrates: metals, alloys, and pure elements:

Little or no C Solubility or Reaction: Cu, Sn, Pb, Ag, and Au, Ge, sapphire, diamond, graphite

C Diffusion: Pt, Pd, Rh, Fe, Ni, and Ti

the substrate acts as a carbon sink, deposited carbon dissolves into the metal surface,

large amounts of C transported into the bulk,

a temporary decrease in the surface C concentration, delaying the onset of nucleation

Carbide Formation: Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Fe, Co, Ni, Y, Al B, Si, SiO₂, quartz, Si₃N₄ also form carbide layers. SiC, WC, and TiC

Applications of diamond films:

Thermal management - a heat sink for laser diodes, microwave integrated circuits active devices mounted on diamond can be packed more tightly without overheating

Cutting tools - an abrasive, a coating on cutting tool inserts CVD diamond-coated tools have a longer life, cut faster and provide a better finish than conventional WC tool bits

Wear Resistant Coatings -protect mechanical parts, reduce lubrication gearboxes, engines, and transmissions

Optics - protective coatings for infrared optics in harsh environments, ZnS, ZnSe, Ge: excellent IR transmission but brittle the flatness of the surface, roughness causes attenuation and scattering of the IR signal

Electronic devices - doping, an insulator into a semiconductor *p*-doping: B₂H₆ incorporates B into the lattice doping with atoms larger than C very difficult, *n*-dopants such as P or As, cannot be used for diamond, alternative dopants, such as Li

Laser-Enhaced CVD



 $Si(O_2CCH_3)_4 \rightarrow SiO_2 + 2 O(OCCH_3)_2$

LPCVD of ZnO from Aminoalcoholates



LPCVD of ZnO from Aminoalcoholates



CVD of YF₃ from hfacac Complex



ALD Atomic Layer Deposition

Special modification of CVD Method for the deposition of thin films Film growth by cyclic process

4 steps:

1/ exposition by1st precursor
2/ cleaning of the reaction chamber
3/ exposition by 2nd precursor
4/ cleaning of the reaction chamber



ALD Atomic Layer Deposition

Cycle repetitions until desired film thickness is reached

1 cycle: 0.5 s – several sec. thickness 0.1- 3 Å

Self-Limiting Growth Mechanism High reactivity Formation of a monolayer

Control of film thickness and composition Deposition on large surface area

ALD vs. CVD Comparison

ALD Carried out at room temperature

Control over number of deposited layers = film thickness

Reactor walls inactive – no reactive layer

Separate loading of reactive precursors

Self-limiting growth

Precursor transport to the reaction zone does not have to be highly uniform (as in CVD)

Solid precursors

ALD vs. CVD Comparison



Figure 2. Cross-sectional SEM images for a 300-nm Al₂O₃ film (a) and a 14-nm TiN film (b) deposited on a patterned silicon substrate.

Precursor Properties

Selection of suitable combination of precursors

Molecular size influences film thickness

Gases, volatile liquids, solids with high vapor pressure

Typical precursors:

<u>Metallic</u> - halogenides (chlorides), alkyls, alkoxides, organometallics (cyclopentadienyl complexes), alkyl amides

<u>Nonmetallic</u> - water, hydrogen peroxide, ozone, hydrides, ammonia, hydrazine, amines

Precursor Properties

Thermally stable

Must react with surface centers (hydroxyl groups on oxide surface)

Thermodynamics

Kinetics

Mechanisms

Examples of ALD



Examples of ALD

DRAM capacitors (Ba,Sr)TiO₃ – Sr and Ba cyclopentadienyl compounds and water as precursors

Nitrides of transition metals TiN - TiCl₄ and NH₃ TaN - TaCl₅/Zn/NH₃ WN - WF₆ and NH₃ WC_xN_y

Examples of ALD

Metallic films

Difficult by ALD: metal surface has no reaction sites, low reactivity with reducing agents

W - WF₆ and Si₂H₆

Ru, Pt - organometallic precursors and oxygen applies to all precious metals capable of catalytic dissociation of O₂

- Ni, Cu metal oxide reduction by hydrogen radicals formed in plasma
- Al direct reduction of AlMe₃ by H radicals from plasma

Precursors: trimethylalane, tris(tert-butoxy)silanol Deposition of amorphous SiO₂ and nanolaminates of Al₂O₃ 32 monolayers in 1 cycle

Applications: microelectronics optical filters protective layers (against diffusion, oxidation, corrosion)



C, D: alkoxide - siloxide exchange



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E: elimination of isobutene = formation of -OH



F: elimination of butanol = condensation



G: elimination of water = condensation



Repeat Step A





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