INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
34100 TRIESTE (ITALY) - P.O.B. 586 - MIRAMARE - STRADA COSTIERA 11 - TELEPHONE: 2240-1
CABLE: CENTRATOM - TELEX 460392 - I

SMR/388 - 51

SPRING COLLEGE IN MATERIALS SCIENCE
ON
'CERAMICS AND COMPOSITE MATERIALS'
(17 April - 26 May 1989)

"CERAMIC COATING"

A. ATKINSON
Harwell Laboratory
Materials Physics and Metallurgy Division
Oxon, Didcot OX11 0RA
United Kingdom

OBJECTIVES

* To give an overall impression of the applications, fabrication and properties of ceramic coatings.
* To illustrate this with specific examples.
* To give an appreciation of the advantages and disadvantages of different coating methods.
* To point out limitations in understanding and technology and the efforts that are being made to remedy these.

THE LECTURES

1 PROPERTIES OF COATINGS

Microstructure, composition, thickness, stress, adhesion.

2 PARTICULATE COATINGS

Tape casting, screen printing, glazing, electrophoresis, spraying, sol-gel.

3 PHYSICAL VAPOUR DEPOSITION

Evaporation, sputtering, laser ablation, ion-beam.

4 CHEMICAL DEPOSITION

Chemical vapour deposition, thermal reaction, reactive pvd.

SUMMARY

Table I: Preparation and Applications of Plasma-Deposited Materials (Examples)

Material	Application	Starting Materials	References
a-Si:H	semiconductor devices, photo voltaics	SiH_4/H_2	5
Si_3N_4 and SiON	passivation layers, lenses, masks	SiH_4/N_2 or $SiCl_4/NH_3$	6,7
SiC	hard coatings, electronics	SiH_4/hydrocarbon or TMS	8,9
SiO_2	passivation layers, optics, fibers	$SiCl_4/O_2$	10,11,12
$SiO_{2-x}F_x$	optical fibers	$SiCl_4/C_2F_6/O_2$	11
GeO_2	optical fibers	$GeCl_4/O_2$	10,11,12
TiN	wear resistant coatings, barriers	$TiCl_4/NH_3$	13,14
TiC	wear resistant coatings	$TiCl_4$/hydrocarbons	15
TiO_2	optics, filters	Me-organics or $TiCl_4/O_2$	16,17
BN	hard coatings, electronics, masks	BCl_3/NH_3 or diborane/N_2	18
BC	wear resistant coatings	diborane/hydrocarbon	19
a-C:H, a-C diamond	hard, low-friction protective coatings, optics, acoustics, electronics,	hydrocarbons	20
	microwave devices, windows, masks	hydrocarbons, alcohols, CO/H_2	21,22,23
ThO_2/W	high power cathodes	WF_6/organometallic Th compound	24

P K Bachmann, G Gärtner and H Lydtin, MRS Bull. XIII(12), 1988, 52.

Table 1. Coating Process Comparison

	Coating technique							
Characteristic	Slurry & fusing	Thermal spraying	Electron beam vapor deposition	Ion-plating	Sputtering	Chemical vapor deposition	Sol-gel	Chemical conversion
Material capability	Nearly unlimited	Anything that melts	Limited to simple compositions	Nearly unlimited	Nearly unlimited	Limited by available precursors	Limited by available chem. precursors	Limited by substrate compositions
Nature of process	Spraying, dipping, brushing	Spraying	Vacuum evaporation	Vacuum plasma	Vacuum plasma	Gaseous deposition	Liquid spraying, dipping, brushing	Pack diffusion
Temperature of substrate	Low to high	Low	Low to high	Low to high	Low to high	Moderate to high	Low to moderate	High
Thickness/layer	Low to moderate	Low to high	Low to high	Low to high	Low to high	Low to high	Low	High
Thickness uniformity	Good	Good	May vary	Good	Fair to good	Good to excellent	Good to excellent	Good to excellent
Deposition rate	High	High	Moderate	Moderate	Low	Low	Low	Low
Configuration limitation	Simple	Simple	Simple	None	Simple	None	None	None
Masking difficulty	Simple	Simple	May vary	Difficult	Difficult	Difficult	Simple	Difficult
Size limitations	None	None	Vacuum chamber	Vacuum chamber	Vacuum chamber	Chamber	None	Furnace size
Equipment required	Spray guns, brushes, ovens	Plasma spray guns, powder feeders, power supplies	Vacuum chamber & heat source	Vacuum chamber, high voltage supply & heat source	Vacuum chamber, high voltage supplies	Chamber, gas supply, heat source	Spray guns, baths, ovens	Ovens, retorts

From T E Schmid and R J Hecht, Ceram. Eng. Sci. Proc. 9, 1988, 1079

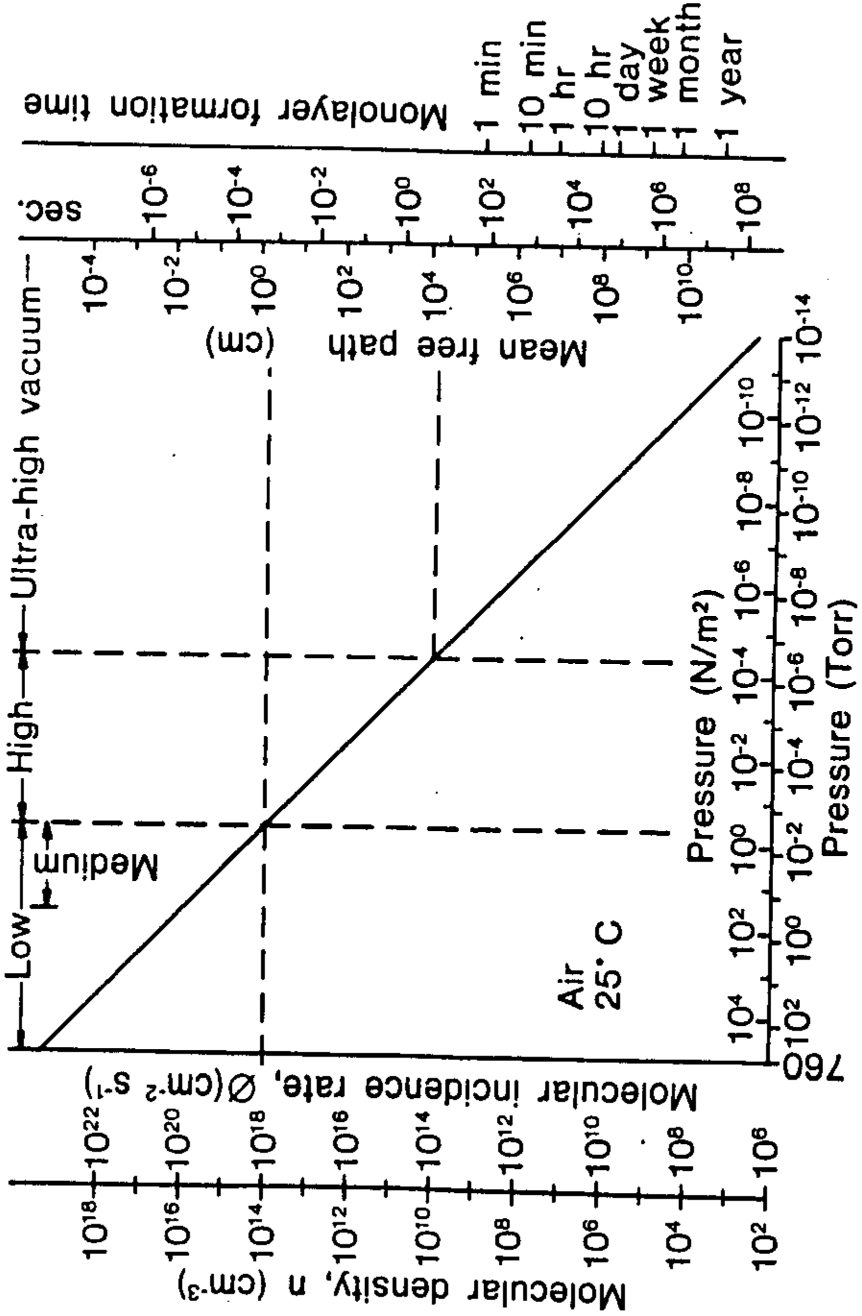

Fig. 21
Relationship of several concepts defining the degree of vacuum [225].

Diode Sputter Deposition

Principle of operation	Ion impact induced collision cascade leading to the ejection of a target atom.
Pressure range	8 - 25 millitorr
Modes of operation	D.C., R.F., bias, reactive, triode.
Deposition temperature	LN_2 to 650°C (unless a special heater is used)
Typical deposition rate	0.25 microns hour $^{-1}$ (unheated subs.)) r.f.) reactive 0.15 microns hour $^{-1}$ (heated at 350°C)) oxide) process
Uniformity	better than 5%

COMMENTS

Reasonably slow technique, that induces a high heating effect into the substrates due to target and substrate secondary electron bombardment of the growing film. One can retro-fit a magnetron source or an ion beam system. Reactive gaseous sources can be piped into the system.

Magnetron Sputtering

Principle of operation	Ion impact induced collison cascade leading to the ejection of a target atom. Magnetic field causes enhanced ionization effect near to target resulting in a more efficient erosion process (Assume a fixed magnet field strength of 250 gauss).
Pressure range	1 - 20 millitorr
Modes of operation	D.C., R.F., bias, reactive
Deposition temperature	LN_2 to 650^{0}C. (unless a special heater is used)
Typical deposition rate	greater than 5 microns hour^{-1} (r.f. reactive oxide process)
Uniformity	better than 5%.

COMMENTS

Very versatile process technique.

High rate deposition process. Target usage efficiency is about 40%. With this technique one can very nearly sputter anything, especially metals, oxides, alloys, compounds, etc. from powder or solid targets.

This technique has also been used for the selected area epitaxy of iron-garnet films for integrated magneto-optic light switch array applications. Also high quality indium antimonide has been grown using a technique called metal-organic magnetron sputtering, (MOMS).

This system can be run as a diode sputtering facility by merely taking out the permanent magnets from behind the target material. One can easily retro-fit an ion beam source or an electron-beam evaporation source into the same vacuum chamber.

Ion Beam Deposition

Principle of operation	Energetic particle bombardment: Direct deposition or sputter ejection.
Pressure range	10 to 0.01 millitorr
Modes of operation	Direct ion beam deposition Ion beam sputtering Dual source sputtering Ion assisted coatings
Source types	Kaufmann, cold cathode, duoplasmatron, Freeman, ionized cluster beam.
Deposition temperature	LN_2 to 300^{0}C (unless a special heater is used)
Typical deposition rate	$\geq$ 4.0 microns hour^{-1}. (oxide process) Specific systems have been designed which will give very much higher deposition rates.
Uniformity	better than 5%.

COMMENTS

Easily maintained system. Complement ion assisted coating initiative at Harwell. With this technique one can have:

1. Independent control of ion energy and current density.
2. Isolation of substrates from ion generation process.
3. Narrow ion energy spread.
4. Low background pressure (hence low contamination).
5. Control over the angle of ion impact.

This technique has been used to increase the density and refractive index of both Al_2O_3 and Ta_2O_5 which are used as anti-reflection coatings on

Ion Plating

Principle of operation	Surface bombardment with energetic species during film growth.
Pressure range	10 to 0.01 millitorr
Modes of operation	r.f. bias, d.c. bias, e-beam, sputtering, neutral ion beam.
Deposition temperature	LN_2 to 650°C (unless using a special heater)
Typical deposition rate	>1 micron hour^{-1} (oxide process)
Uniformity	better than 2%.

COMMENTS

This technology can use a plasma or ion beam as the source of ions. The deposition source is usually electron beam / thermal evaporation or magnetron sputtering. Mutually compatible with most deposition technologies. PECVD is essentially an ion plated chemical vapour deposited layer process.

Chemical Vapour Deposition

Principle of operation	Thermal molecular breakdown; plasma assisted; photon assisted etc.
Pressure range	ATM to 10^{-3} torr.
Modes of operation	Chemical Vapour Deposition, CVD; Metallo Organic Chemical Vapour Deposition, MOCVD; Plasma Enhanced Chemical Vapour Deposition, PECVD; Laser Chemical Vapour Deposition, LCVD; Photon assisted Chemical Vapour Deposition, PCVD; Low Pressure Chemical Vapour Deposition, LPCVD
Deposition temperature	R.T. to > 1,000°C.
Typical deposition rates	200Å min^{-1} MOCVD TiO_2 2,000Å min^{-1} PECVD SiO_2 150Å min^{-1} PCVD SiO_2
Uniformity	better than 5%

COMMENTS

Source materials for Chlorine based processes need special handling due to corrosive by-products. Metallo-organic sources tend to be hygroscopic and form precipitates at source, they need to be handled under an inert atmosphere. For specific deposition systems the equipment can be very expensive, i.e. GaAs or epitaxial silicon technology.

Mutual compatibility is low for this technology in that ion beams and magnetron sources are not easily retrofitted in the deposition chamber.

BIBLIOGRAPHY

General

1. "Deposition Processes Part 1"; MRS Bulletin, XIII (11), November 1988.

2. "Deposition Processes Part 2"; ibid, December 1988.

3. "High Technology Ceramic Coatings - Current Limitations/ Future Needs"; T E Schmid and R J Hecht, Ceram. Eng. and Sci. Proceedings 9, 1988, 1089.

4. "Ceramic Coatings via PVD"; P A Dearnaley and T Bell, ibid, 1137.

5. "Deposition Technologies for Films and Coatings"; R F Bushah et al., Noyes, Park Ridge, 1982.

Properties

1. "Cracking and Decohesion of Thin Films"; A G Evans, M D Drory and M S Hu, J. Mater. Res. 3 (1988) 1043.

2. "A Review of Adhesion Test Methods for Thin Hard Coatings"; J Valli, J. Vac. Sci. Technol. A, 4 (1986) 3007.

3. "Surface Analysis of Oxide Films"; D R Baer and L S Dake, in 'Oxidation of Metals and Associated Mass Transport' MA Dayananda et al, The Metallurgical Society, Warrendale, 1987, 185.

Particulate Methods

1. "Sol Gel Technology"; L C Klein, Noyes, Park Ridge, 1988.

2. "Ceramic Glazes", C W Parmelee and C G Harman, Cahners, Boston, 1973.

Physical Processes

1. "Property Modification by Low Energy Particle Bombardment Concurrent with Film Growth"; J J Cuomo and S M Rossnagel, Nucl. Intr. Methods, B19/20, 1987, 963.

2. "Ion-Based Methods for Optical Thin Film Deposition"; P J Martin, J. Mater. Sci., 21 (1986), 1.

3. "Ceramic Coatings by PVD"; D S Rickerby and A Matthews, to appear in Rev. Powder Met. Phys. Ceram.

Chemical Processess

1. "Oxide/Metal Interface and Adherence"; Special Issue of Mat. Sci. Tech. 4 (5), 1988.

2. "Preparation and Properties of AlN Films Using an Organometallic Precursor"; LV Interrante et al, J. Electrochem. Soc. 136 (1989) 472.

3. "CVD Films for VLSI"; D Pramanik, Semiconductor International, June 1988, 94.

4. "Transport Processes During the Growth of Oxide Films at Elevated Temperature"; A Atkinson, Rev. Mod. Phys., 57 (1985), 437.

SuH - AA295 - WS