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SPRING COLLEGE IN MATERIALS SCIENCE

ON

"METALLIC MATERIALS"

(11 May - 19 June 1987)

SURFACE TREATMENT AND COATINGS OF MATERIALS
(Part I)

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LECTURE 1

PLASMA PROCESSING

Abstract

The use of plasmas in the deposition of thin films is increasing. In particular, plasmas are either used as heat sources or as sources of highly reactive chemical species. In the former category, plasmas are often used as heat sources to melt powder particles in the deposition of coatings using thermal spraying technologies, whilst in the latter category plasmas are used in plasma assisted CVD reactors and dry etching equipment to either deposit thin films at relatively low temperatures or as a means of controllably etching the surface of, for example, semiconductors to produce fine line structures for advanced VLSI devices. This lecture will address the many ways in which plasmas can be used.

Slide 1 — TITLE SLIDE : Plasma Processing

Slide 2 — Schematically, by applying an electric field to a gaseous mixture, it is possible to excite the gas such that it produces a number of active species. In general terms, these can be categorised as an electron gas, a molecular gas, an ion gas and an atom gas. These interact dynamically under the influence of the electric field to give either homogeneous deposition from the gas phase as particles or heterogeneous deposition at substrates to give coatings.

Slide 3 — The heterogeneous deposition steps are illustrated in this slide. A reagent molecule can deposit on the surface by either non-dissociative chemisorption or dissociative chemisorption. Surface diffusion is an important prerequisite for the uniform coverage of the surface. As a result of such chemisorption, the reagent molecule can interact with the substrate to form a product molecule, which may adhere to the substrate also. Alternatively, the product molecule may desorb as a volatile species.

Slide 4 — A simple method by which a plasma can be created is illustrated in this slide. A planar cathode-anode arrangement is used to create an electric field across the gas phase. As a result, three main regions may be identified in the plasma: the cathode dark space, the negative glow and the anode sheath. The active species (i.e. electrons and ions) are accelerated either to the anode or the cathode. As a result, the ions especially bombard the surface of substrates and produce what are known as sputtered atoms.

Slide 5 — Sputtering is often an important by-product of plasma processing since it enable atoms to be removed from one solid surface, often reacted in the plasma phase, and then deposited as a compound onto a substrate of interest to give a coating. This slide shows that there is an optimum angle of incidence to produce a maximum in the sputtering yield, which is defined as the number of atoms sputtered per incident ion.

Slide 6 — In terms of the plasma regions which are useful for processing materials, a simple insight can be gained by measuring the potential across a planar diode arrangement as in the previous slide but 2 v. the current between the anode and cathode. This slide shows that sputtering processes normally occur in the region 300-800V at a current of approximately 10^{-2}A. They operate in this region since current and voltage can both increase independently of each other. Plasma spraying operates in the region of approximately 100A and 100V.

Slide 7 — LINK SLIDE : "Plasma Spraying"

Slide 8 — Schematically, plasma spraying is based upon the creation of a DC arc between a tungsten cathode and a copper anode. Due to the thermal pinch effect, the plasma is compressed through a narrow orifice a few mm in diameter to form a plasma flame. Powder particles are either internally or externally injected into the plasma where they are melted and accelerated towards a substrate to be coated.

Slide 9 — A typical example of a plasma spraying facility is shown in this slide. Ceramic particles are being processed through the highly luminous plasma flame and are being deposited onto a rotating tube to form a coating.

Slide 10 — Typical examples of materials which can be coated using this technique are shown in this slide and include gas turbine blades, diesel engine valves and free-standing artefacts such as cones and crucibles.

Slide 11 — This slide shows a typical cross-sectional microstructure of a plasma sprayed coating on a gas turbine blade. The coating is a zirconia thermal barrier approximately 0.4mm thick. It is interesting to note the uniformity of coating thickness around the blade.

Slide 12 — One of the problems associated with plasma spraying that we will address in subsequent lectures is the significant residual stresses which can be built up in the deposited material as shown in this slide of a free-standing ceramic tube which has failed by residual stress cracking.

Slide 13 — A recent innovation in plasma spraying has been the inclusion of the plasma system inside a soft vacuum (approximately 20 torr) chamber as shown in this slide. The plasma gun is carried out on a 5 axis ASEA robot which gives great dexterity to the shape of components which can be coated.

Slide 14 — The advantages to be gained from plasma spraying under vacuum conditions are significant. This slide shows an immediate benefit in that the environmental breaking force on the plasma flame is much reduced and therefore the flame is both longer (approximately 12") and more laminar in its flow.

Slide 15 — Consequently, it is possible to spray under much more controlled conditions and, because the environment in the chamber can be controlled (by the inclusion of inert gases, for instance), the ability to control the chemistry of the deposited layers is greatly enhanced.

Slide 16 — LINK SLIDE : "Chemical Vapour Deposition"

Slide 17 — In chemical vapour deposition, precursor gases are mixed and then metered into a CVD reactor which operates at high temperatures. As a result of the high temperature chemical reaction, the gases form solid phase coatings on substrates and the gaseous products are exhausted.

Slide 18 — A typical CVD reactor is shown in this slide where reactant gases enter at the bottom of the vessel and are carefully directed over a series of trays, upon which sit specimens to be coated, for example, cutting tools. Because it is a gas phase process, CVD technology has great attractions from the viewpoint of being able to coat complex substrate profiles.

Slide 19 — This slide shows typical examples of artefacts which can be coated by CVD methods including drills, taps and, perhaps more importantly, cemented carbide cutting tool inserts.

Slide 20 — This slide shows the kinds of materials, components, applications and deposition temperatures used in a number of current examples of the use of wear-resistant coatings produced by CVD.

Slide 21 — There is a need to process at lower temperatures, and this can be achieved in the plasma activated chemical vapour deposition process where a glow discharge is used to create the chemical reactions required at much lower thermal temperatures than in conventional CVD as we noted schematically in this slide.

Slide 22 — It is important to draw simple distinctions between conventional CVD and plasma assisted CVD. These distinctions are summarised in this slide.

Slide 23 — Other important features of the use of plasmas in CVD technology are summarised in this slide.

Slide 24 — This slide shows a schematic representation of PAVD. An RF discharge is used to excite the chemical reaction.

Slide 25 — A close-up photograph of the plasma region shows a number of thread guides being coated with silicon carbide. Plasmas are usually luminous as they are made up from active species such as ions and electrons. When these recombine, light is often emitted.

Slide 26 — This slide is a fracture section of a typical PAVD coating deposited at low temperatures.

Slide 27 — This photograph shows a recent application of PAVD. The plasma coating rig some 2m. long and 20cm. in diameter is operating to deposit silicon dioxide coatings onto advanced gas cooled reactor fuel cans to reduce carbon deposition and oxidation under reactor operating conditions (typically 650°C).

Slide 28 — The beneficial effect of using silica coatings by this technique is shown in this slide where the lower curve represents the oxidation weight gain of the coated material, whereas the upper curve shows the oxidation weight gain of the uncoated material.

Slide 29 — Other examples of the use of plasma processing are shown in this slide where fibres and thread guides have been coated with advanced ceramics such as silica carbide. It should also be noted that chemical vapour deposition in general can be used to produce powders as shown in the bottom right hand corner of this slide.

Slide 30 — LINK SLIDE : "Physical Vapour Deposition"

Slide 31 — Physical vapour deposition processes can be broadly classified into evaporation dependent and sputtering dependent processes, and examples of each class are listed on this slide.

Slide 34 — Sputtering is particularly useful for the deposition of multiphase materials since it has the ability to transfer elements across into the vapour without significantly altering the composition of the coating.

Slide 35 — However, during sputtering, it is important to recognise that different atomic masses can sputter at different rates.

Slide 36 — An example of the deposition of multiphase alloys by sputtering is shown in this slide where advanced alloys are deposited for oxidation and corrosion resistance.

Slide 37 — Another use of plasmas is in microcircuit manufacture. As the density of microelectronic circuits increases, it is necessary to fabricate extremely fine (less than submicron) structures in the surfaces of semiconductor and associated materials. This slide gives a typical optical view of the very latest circuits being designed at Harwell.

Slide 38 — Schematically, it is necessary to consider doping the silicon subnstrate by ion implantation to change its resistivity and therefore promote the formation of solid state electronic junctions. Classically, the way in which this has been done has been to wet etch silicon dioxide on top of silicon and then to implant through the etched structure. However, the etchant acts in an isotropic manner as shown on the left of this slide and the degree of lateral etching as opposed to vertical etching can be considerable. The two sets of diagrams on the right of the slide show that using gas phase or plasma etching, it is possible to create high anisotropic profiles in the silicon dioxide where the degree of lateral etching is much reduced.

Slide 39

For these advanced process techniques, plasmas are used as the sources of reactive ions. The specimen to be etched usually sits either within the plasma or on one of two electrodes surrounding the plasma. As can be seen from the lower diagram, ions migrating to the edge of the plasma are rapidly accelerated towards the substrate and there bombard the material to give etching.

Slide 40

Two mechanisms are proposed whereby the plasma species create the etched microstructure. The first involves significant radiation damage which, it is argued, enhances the chemical reactivity of the surface and therefore the ease with which it can be etched. The second mechanism proposes the formation of a polymer side-wall layer which inhibits etching in that direction as shown in the right hand diagram.

Slide 41

This slide shows a number of typical plasma etching reactors which can either be planar in geometry or cylindrical.

Slide 42

As well as being able to etch silicon materials, it is important to note that in modern-day microelectronic fabrication, conventional materials deposited onto the silicon also need to be etched. This slide shows that a typical material such as aluminium could be etched using chlorinated, brominated or fluorinated gases. However, only the chlorinated gas is suitable since the compound that it forms with aluminium is volatile under plasma processing conditions and can therefore be exhausted in the gas phase, whereas the other two compounds are solids under process conditions.

Slide 43

SUMMARY SLIDE

Plasma processing offers significant advantages over conventional processing techniques in many aspects of industry ranging from basic engineering, through to advanced microelectronics.

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LECTURE 1 : SLIDE 1

Verbal outline of 1st lecture

Methods of coating
Microstructural Aspects of coatings.
Relevant properties of thin films (coatings) in relation to Bulk.
Stresses in films - interface properties - spallation.

PLASMA PROCESSING

OR What PLASMAS can do for you

SIP

Plasma Spraying

Low Press Plasma Spraying

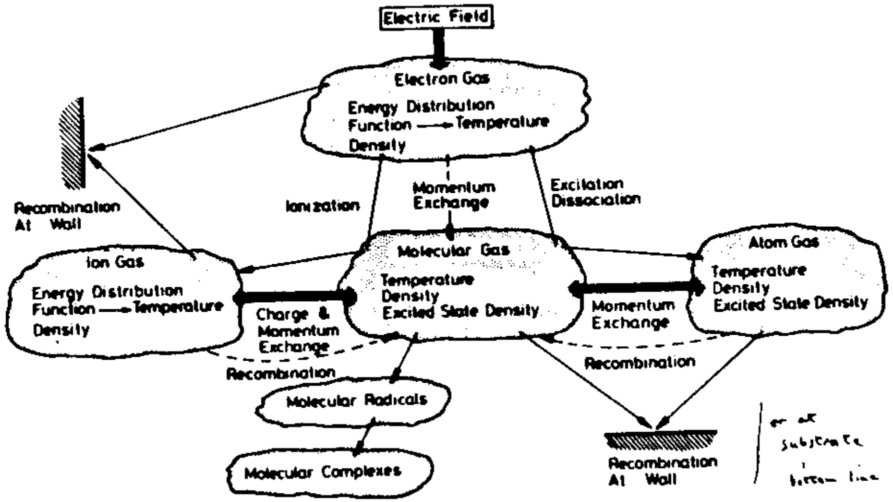
CVD High T

PACVD Low T

PVD < evap / sputtering

Physical

LECTURE 1 : SLIDE 2

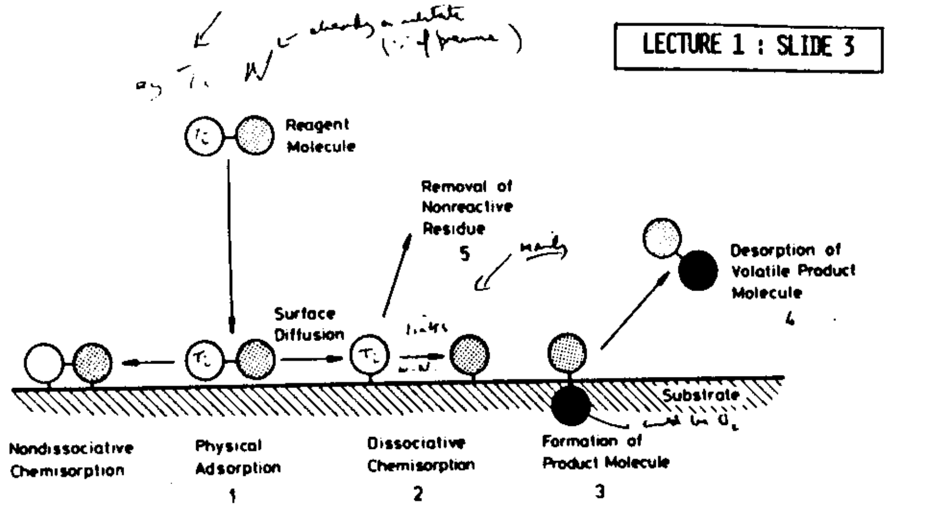


PLASMA DESCRIPTION.

Electron field induces 4 species into plasma.

General Remarks

LECTURE 1 : SLIDE 3

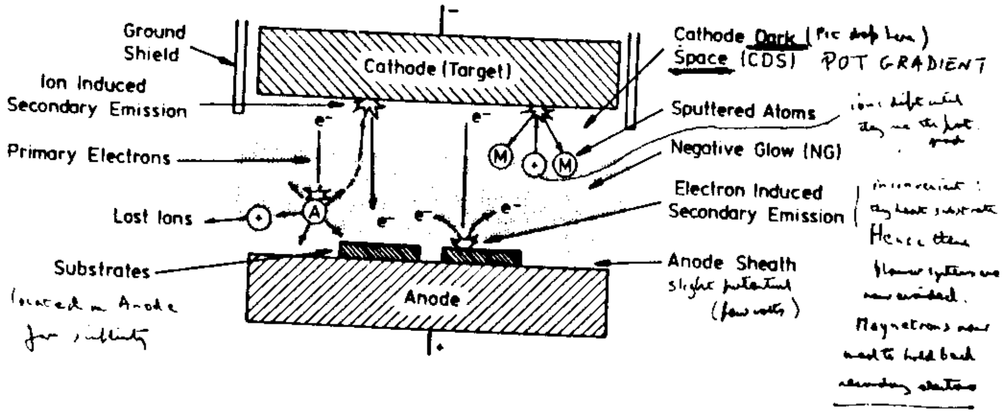


● SUBSTRATE REACTION.

Modes of deposition on substrates

N.B. Surface Diffusion

LECTURE 1 : SLIDE 4



SCHEMATIC REPRESENTATION OF THE PLASMA IN A PLANAR DIODE SPUTTERING SOURCE.

Sputtered atoms drift on to substrate / Basis of SIP

3 main regions in the plasma.

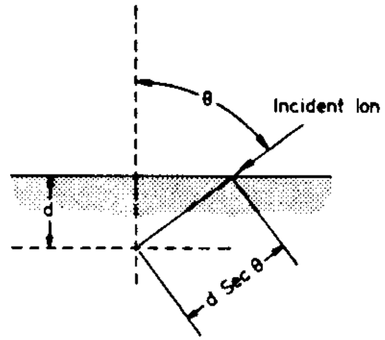
1. Cathode Dark Space.
2. Neg. Glow.
3. Anode Sheath.

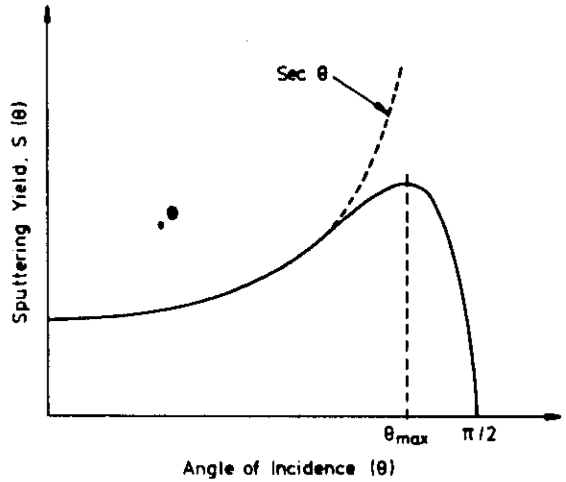
Active species IONS and Electrons accelerated to Anode or Cathode

+ ions reaching Cathode can induce either secondary ē (minor) or sputter atoms of it.

ē hitting substrate w. secondary ē emission merely heat the substrate (minor)

LECTURE 1 : SLIDE 5



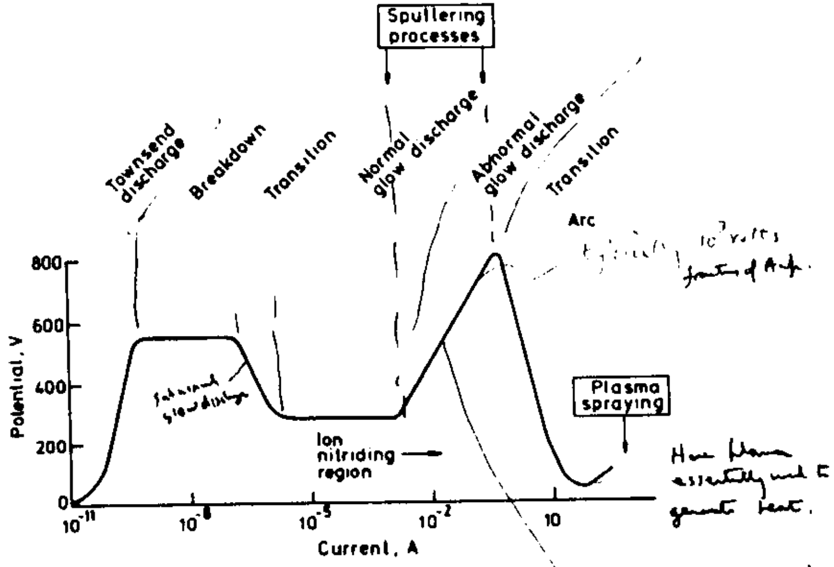


SCHEMATIC DIAGRAM SHOWING VARIATION OF SPUTTERING YIELD WITH ION ANGLE OF INCIDENCE. ION ENERGY CONSTANT.

NB Sputtering efficiency

Scattering of ions by atoms in 'Dark Space' causes strong deviation from normal incidence. Low vacuum is advantage : however plasma impedance means higher voltage. (power supply limitations)

LECTURE 1 : SLIDE 6



Typical voltage versus current characteristics for glow discharge

Work here ∵ only region where we can increase voltage and at same time increase current density

To identify plasma regions that are useful for processing materials.

Sputtering processes normally occur in region 300-800 V w. a current ~ 10^{-2} A

Plasma Spray in region 100A and 100V

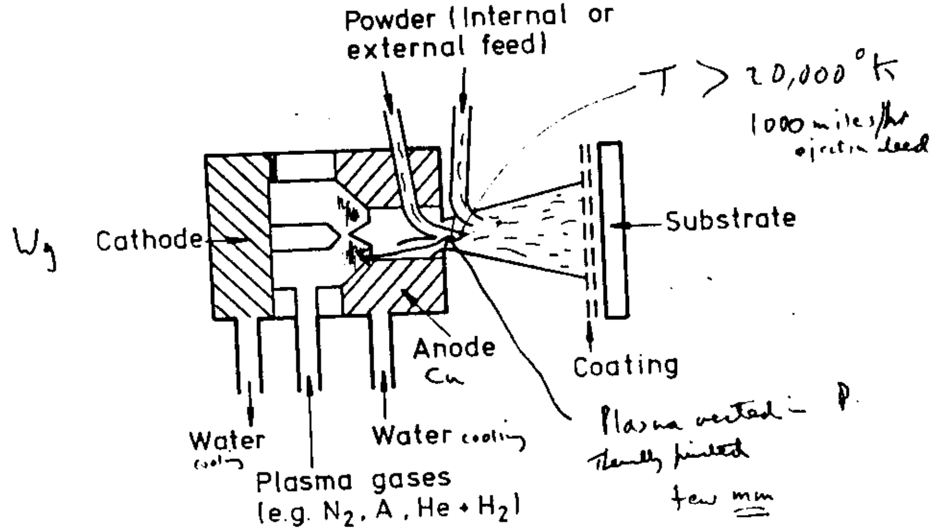
LECTURE 1 : SLIDE 7

PLASMA SPRAYING

NOW ~ > 10 → 100 Amps

10's volts

LECTURE 1 : SLIDE 8



Particles are melted and accelerated.

Too small to heat the substrate

for example at PLASTICS

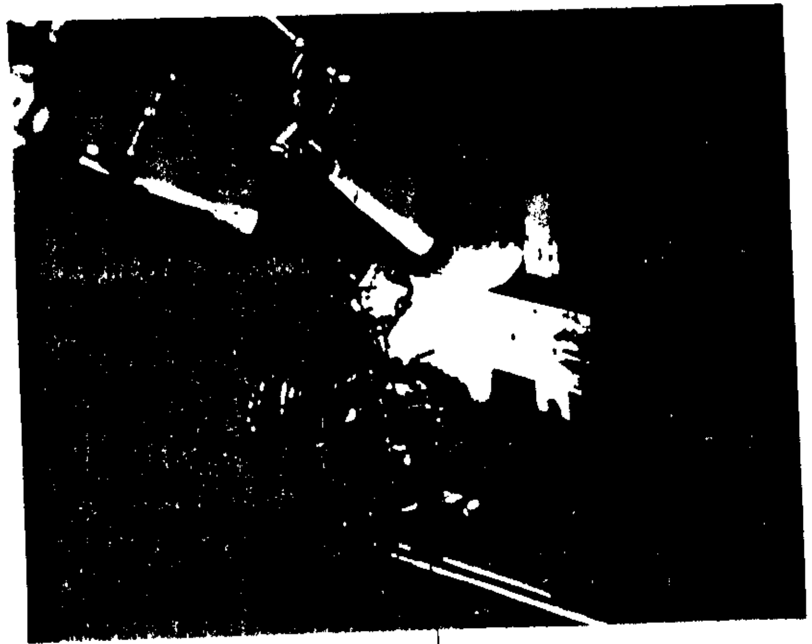
DC Arc. between W cathode + Cu anode creates plasma.

Plasma flame created by compressing the plasma thru narrow orifice

Power injected into plasma. → on to substrate

LECTURE 1 : SLIDE 9

cooling jets

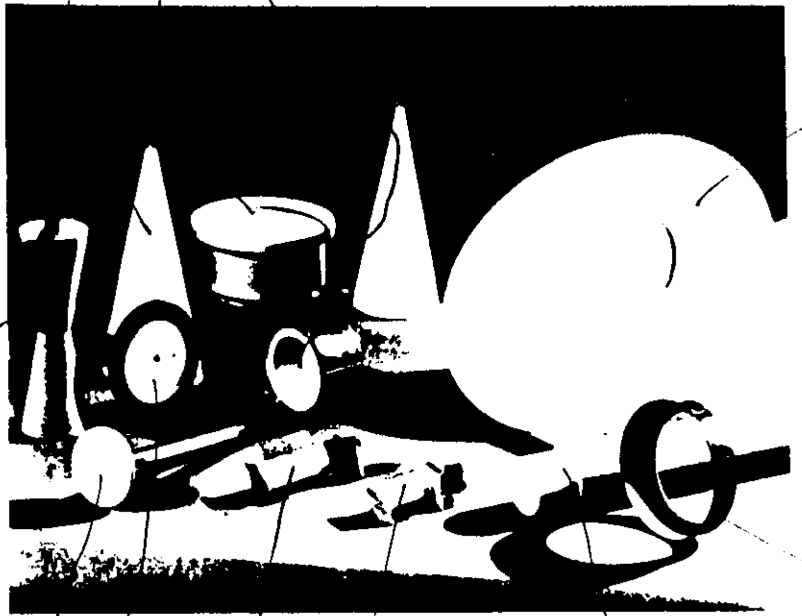


Powder feed

Ceramic powder Al_2O_3

or ZrO_2

LECTURE 1 : SLIDE 10



Radar cones, crucible, Piston crown, radar dome, Premix vessel, Ring segment

T. Barrier C on Engine Valves

Thermal barrier coating on gas turbine blade

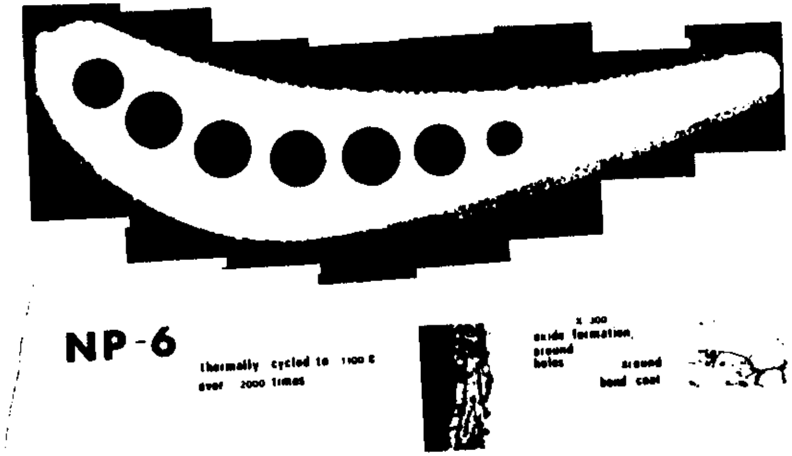
ZrO_2 furnace lines. Sol Gel

powders v. good

Normally rated at 1400°C

P. Sprayed up to 1600°C

LECTURE 1 : SLIDE 11



Gas Turbine blade

ZrO_2 0.4 mm thick.

Very Uniform. Nimonic Super Alloy matched thermal expansion

Note Metal bond coat 1st sprayed on MCrAlYt (Ni) FeCrALY | Fail safe layer

To increase turbine entry T

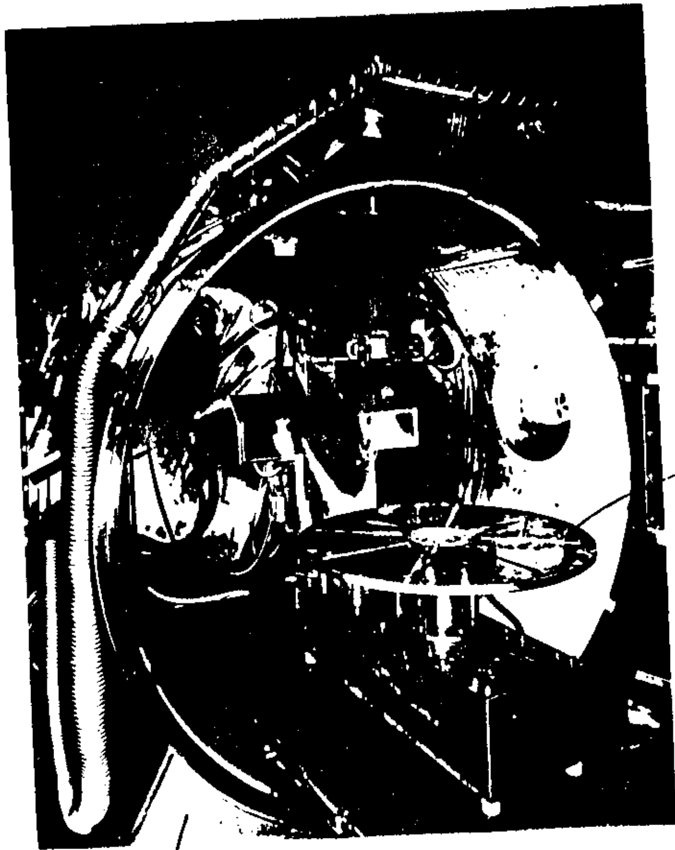
Can drop 100°C across ZrO_2.

LECTURE 1 : SLIDE 12

Problem
addressed later
Residual stress build up in Ceramic tube

Residual stress can wreck coatings

LECTURE 1 : SLIDE 13



multi axis turntable

5 axis ASEA ROBOT AT HARWELL

Any shape can be coated

Low pressure plasma spraying LPPS

Remove atmosphere breaking down a plasma Jet

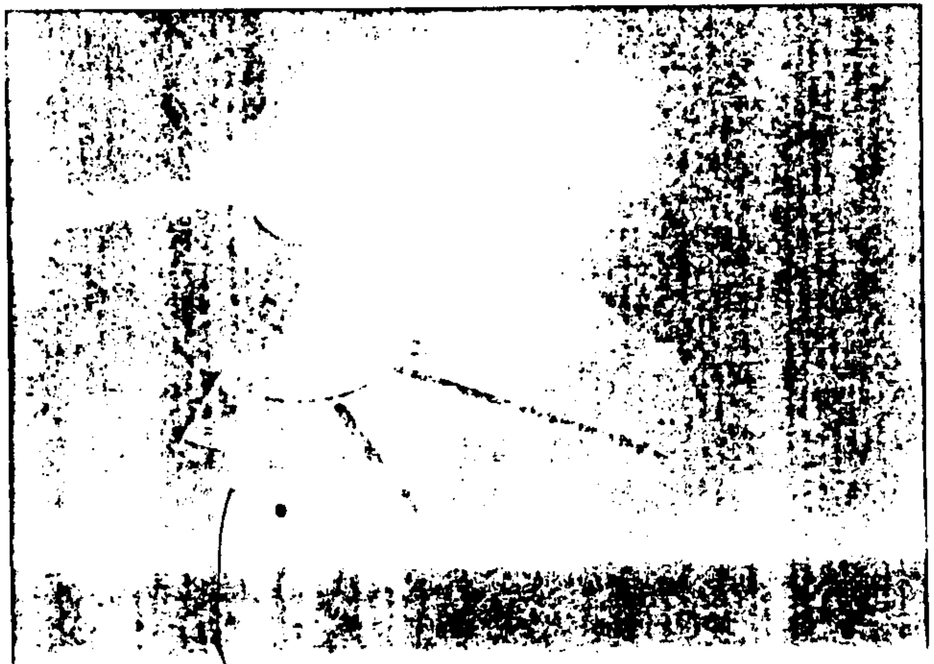
Robot needed

Soft vacuum ~20 Torr

LECTURE 1 : SLIDE 14

14" in low Vac
2-3" in air

LECTURE 1 : SLIDE 15



Note inert gas can be introduced to control environment - chemistry of deposited layers.

Can ION clean substrate prior to spraying

LECTURE 1 : SLIDE 16

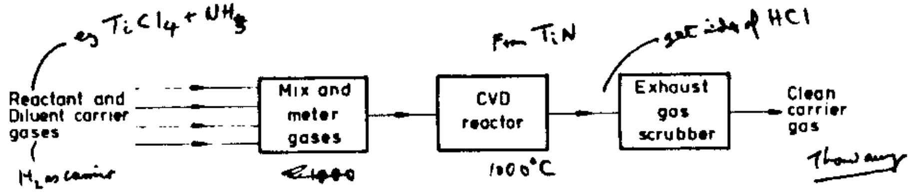
CHEMICAL VAPOUR DEPOSITION

CVD 1st

leading to PACVD

Thermal processes with induced chemical Reactions

LECTURE 1 : SLIDE 17



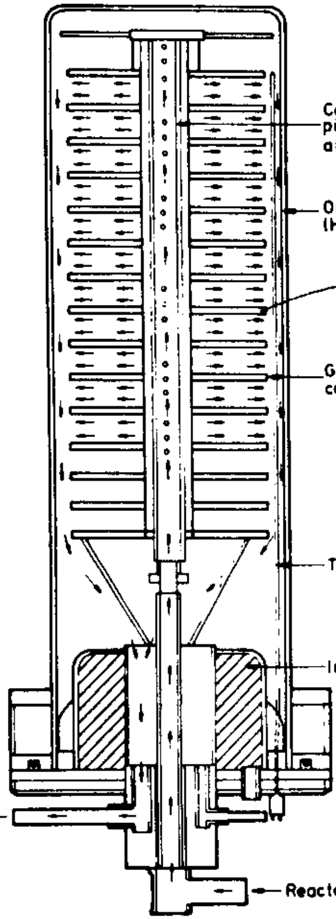
Typical CVD ~~sequ~~ sequence.

Solid phases on substrates.

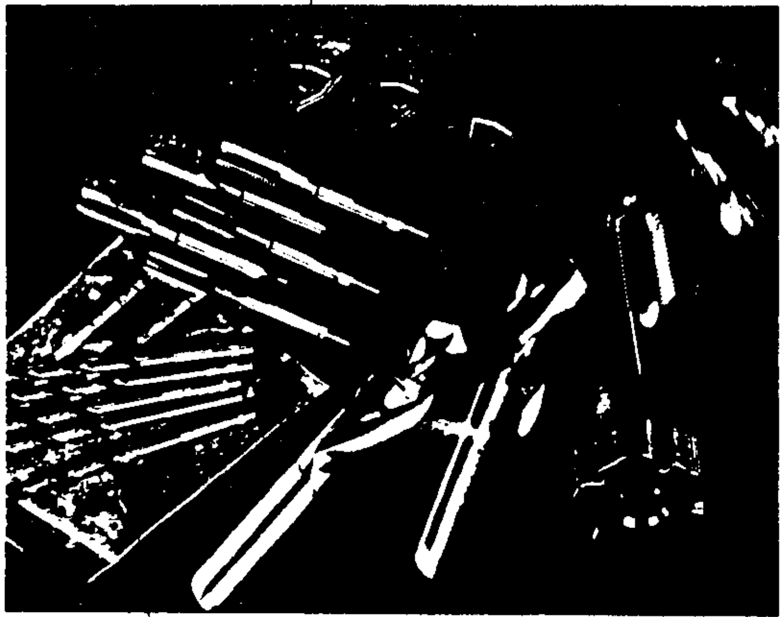
High T chemical Reactions → gases form solid phases

coatings and gaseous products are exhausted.

LECTURE 1 : SLIDE 18



LECTURE 1 : SLIDE 19



retempering needed for NB tool steels

SIP better

Actually SIP is preferable (lower T)

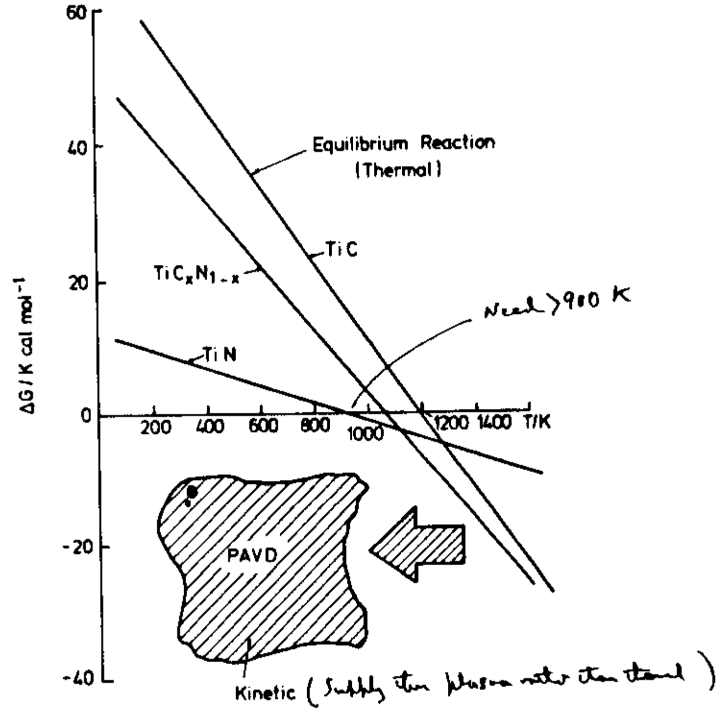
LECTURE 1 : SLIDE 20

CURRENT WEAR RESISTANCE APPLICATIONS OF CVD COATINGS

Coating	Substrate	Temp. of application, °C	Coating thickness, µm	Application
TiC	Cemented carbide	700–1000	5–8	Metal cutting tools
TiC	Chrome steel	700– 800	10	Balls and rings in special duty bearings
TiN	Cemented carbide	700–1000	10	Metal cutting tools
TiC/TiN	Cemented carbide	700–1000	5–8	Metal cutting tools
Al_2O_3	Cemented carbide (TiC underlayer)	850–1100	5–8	Metal cutting tools
W_2C	Steels (Ni interlayer)	400– 700	100	Steels Air plug gauges
WC	Cemented carbide	900–1100	5–8	Wire drawing dies Metal cutting tools

just in

LECTURE 1 : SLIDE 21



ΔG must be negative   Hence Plasma Assisted CVD

SIP needs solid target to sputter from.

NB Energy is gaseous

Multi layer coatings can be produced by switching gas feeds.

CVD

- Driven by Thermodynamics
- Use Equilibrium Constants for Calculation

PACVD

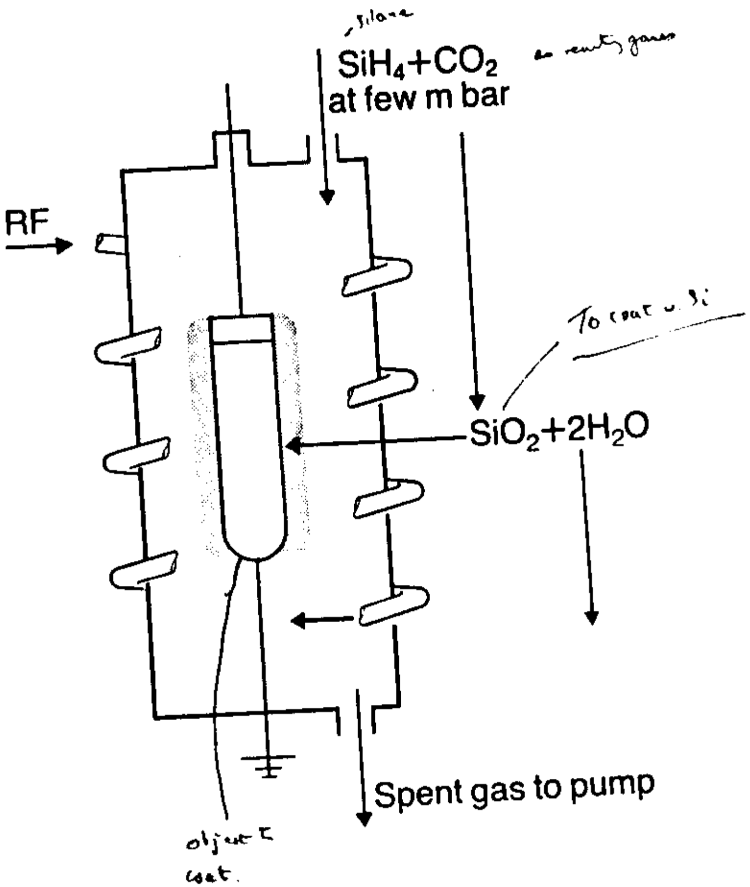
- Driven by Nonequilibrium Plasma Processes
- Guidelines: Collision Cross Sections
  Dissociation Energies
  Ionization Potentials
- More Complex Than CVD
- Often More Forgiving Than ~~P~~ C VD
  (flexible)

PACVD-REACTION KINETICS.

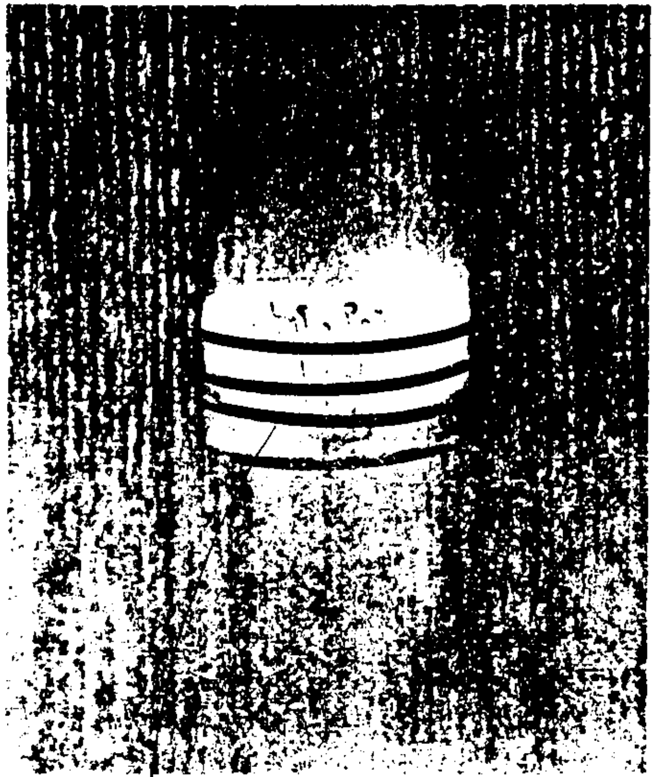
- Deposition at Low Substrate Temperatures (< 300°C)
- Films are Amorphous
- Films Contain Product Gas
- Driven by Kinetic Processes
- Strongly Dependent on Plasma
- Ion Bombardment Important / Bias to stir up substrate (freedom)

PLASMA ASSISTED CVD.

LECTURE 1 : SLIDE 24



LECTURE 1 : SLIDE 25



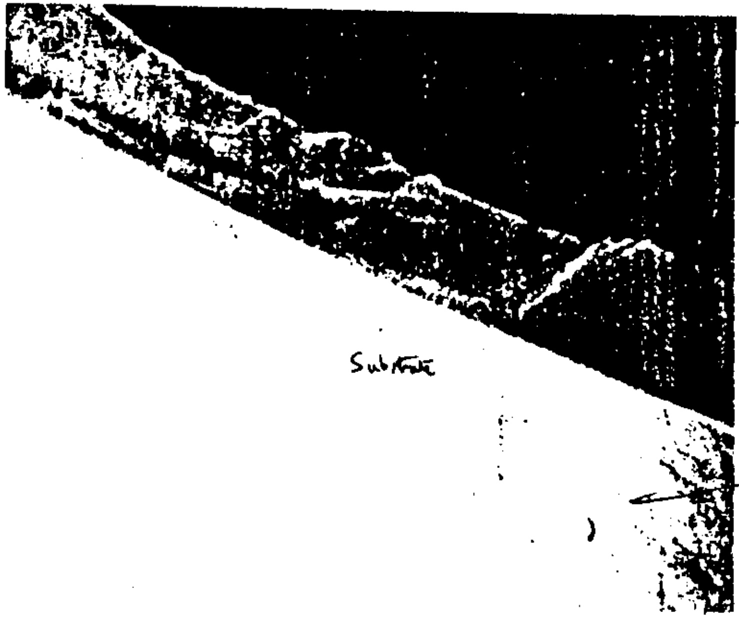
confinement of plasma with r f field

Thread guides for Textile industry

$SiH_4 + CH_4 \rightarrow SiC$

silane methane

LECTURE 1 : SLIDE 26

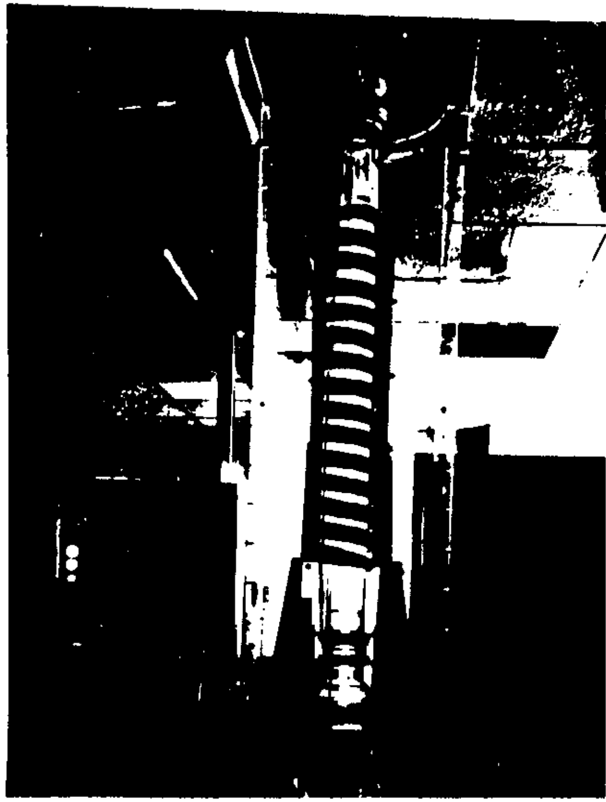


Mo · SiC very hard etc

no third element ... material

Fracture section

LECTURE 1 : SLIDE 27



High T AGR

~ 900°C

Recent Applications of PACVD to AGR fuel pins. Single pin coating. Inhibit C take-up and Oxidation resistance.

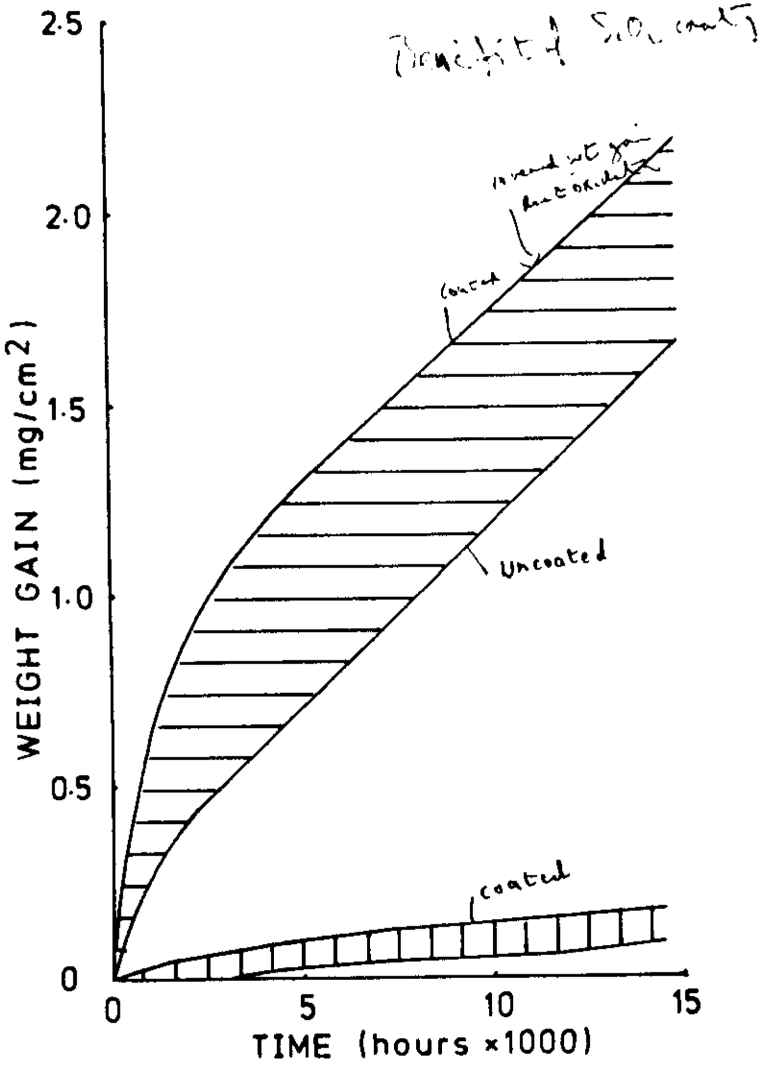
2m

SiO_2 coatings

$SiH_4 + CO_2$

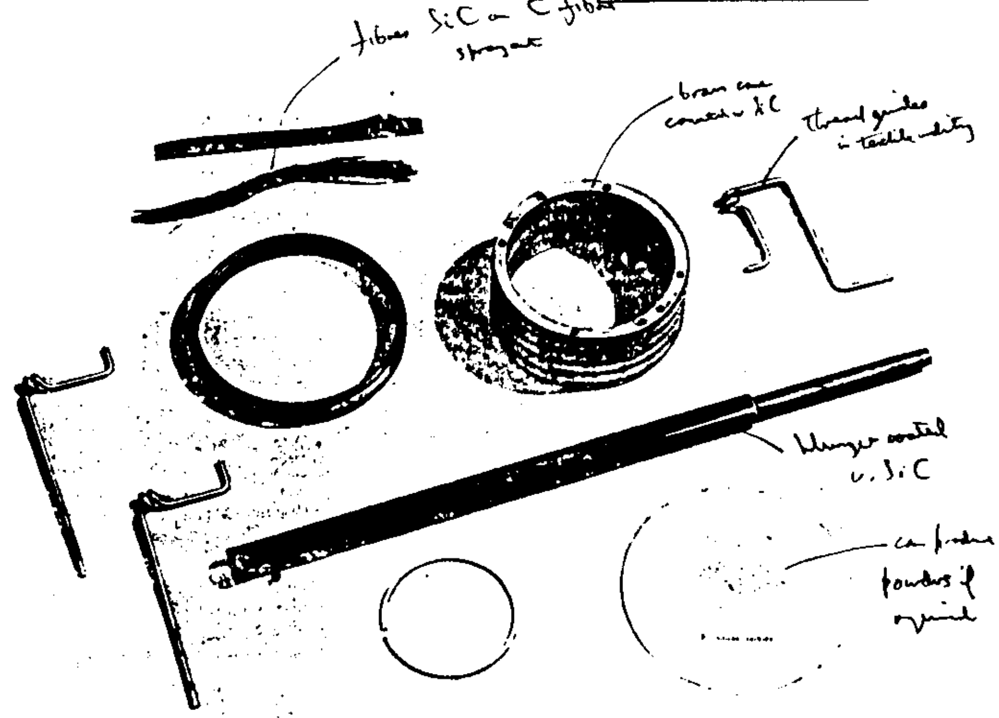
Silane

LECTURE 1 : SLIDE 28



~ 850°C in air

LECTURE 1 : SLIDE 29



Other examples of PACVD

LECTURE 1 : SLIDE 30

PHYSICAL VAPOUR DEPOSITION

creating flux from solid

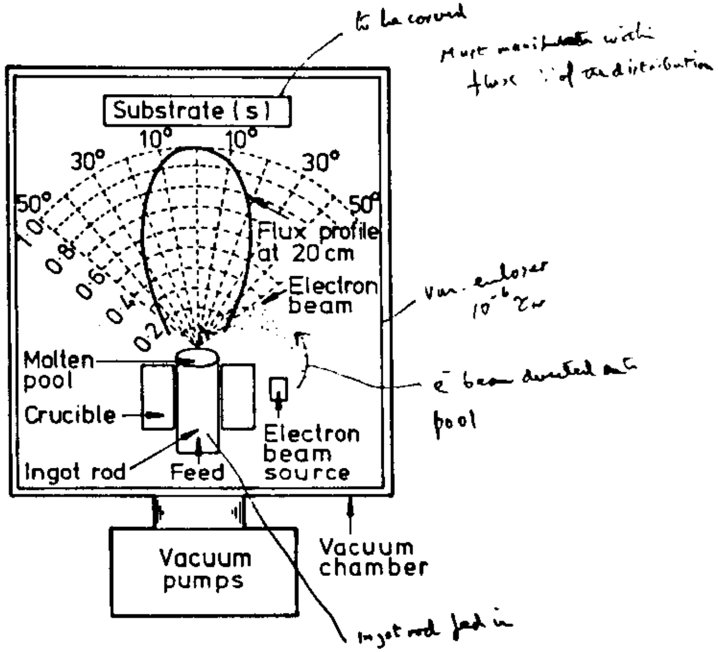
LECTURE 1 : SLIDE 31

PVD process types

PVD – Physical Vap dep.

EVAPORATION DEPENDENT	SPUTTERING DEPENDENT
Electron Beam Evaporation	D.C. Sputtering
Laser Beam Evaporation	R.F. Sputtering
Resistance Heating Evaporation	Magnetron Sputtering
Reactive Evaporation	Triode Sputtering
Activated Reactive Evaporation	Sputter-Ion Plating
	Reactive Sputtering

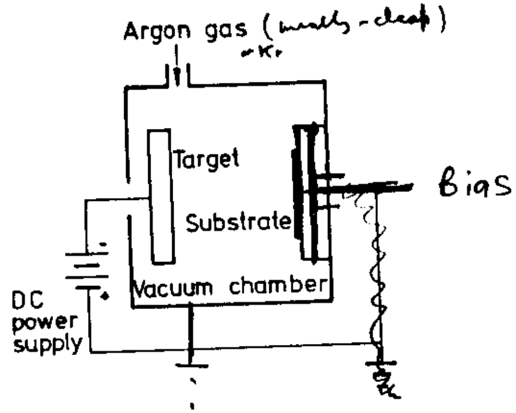
LECTURE 1 : SLIDE 32



Slide 32

In evaporation processes the material required to form a coating is evaporated within a vacuum chamber operating at 10^{-6} - 10^{-5} torr and the sample is manipulated within the vapour cloud. Here, we see the use of an electron beam to form the evaporant flux and it is possible to deposit metals and multiphase alloys by this approach.

LECTURE 1 : SLIDE 33



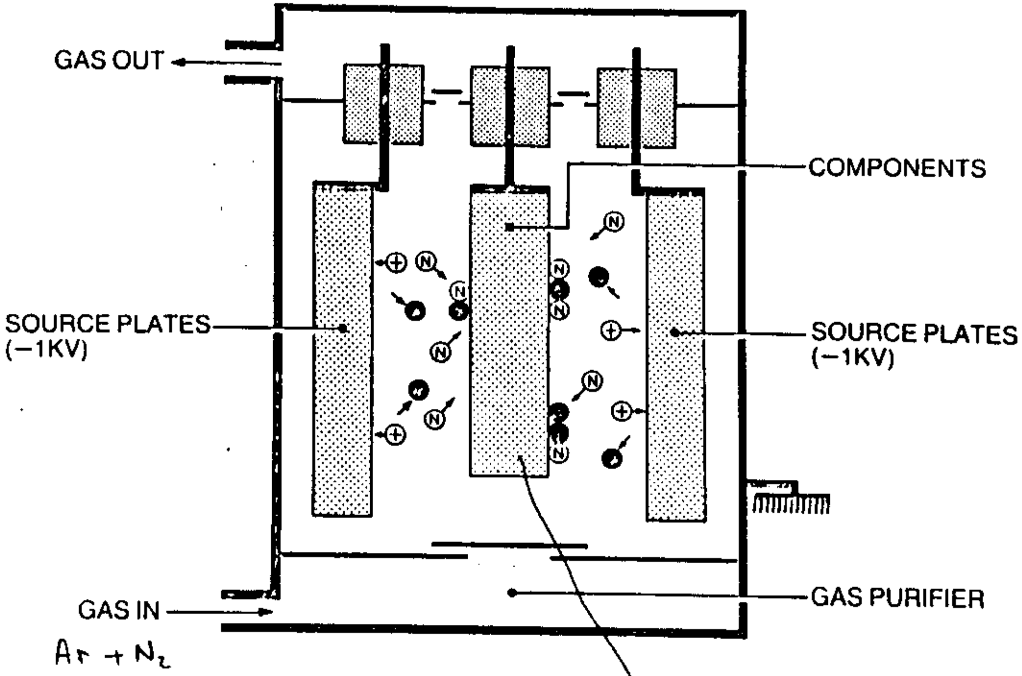
SIP schematic

10^{-3} Torr (soft) vacuum

Slide 33

In sputtering processes it is usual to use argon gas and this is ionised in a glow discharge typically 500V-5,000V DC. Material is eroded from the target and forms the coating on a substrate which may be floating or electrically biased.

LECTURE 1 : SLIDE 34



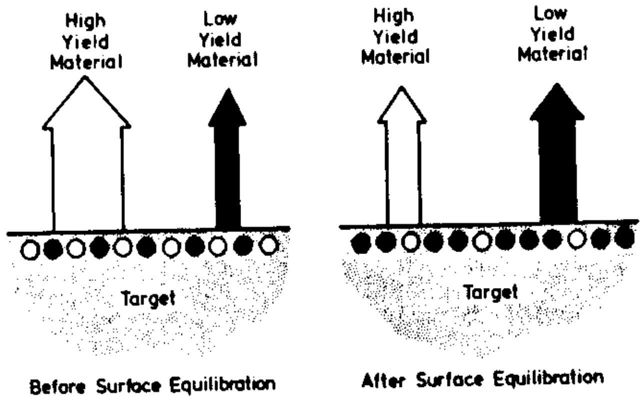
Actual process

Put Ti glue down first
Turn off getter on argon.
Add N_2 to Ar and proceed.

NB
BIAS | Ability to put BIAS on samples important
(accelerator)
≈ 100 V

SIP. useful for deposition of multiphase materials
Can transfer elements across without altering coating composition

LECTURE 1 : SLIDE 35

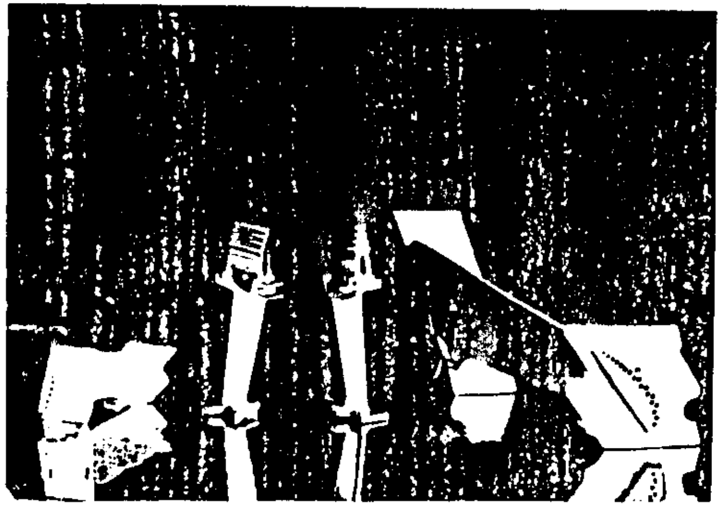


Rapid bulk sputtering (Self regulating)

SCHEMATIC ILLUSTRATION OF THE MODIFICATION IN SURFACE COMPOSITION THAT OCCURS DURING THE SPUTTERING OF A HOMOGENEOUS MULTI-SPECIE MATERIAL IN WHICH THE SPECIES HAVE SIMILAR ATOMIC MASSES.

Can sputter bone out of original implants

LECTURE 1 : SLIDE 36



Oxydation - Corrosion resistant coating for Gas Turbines

CoCrAlYt coating. Again to increase Turbine entry temperature.

High strength (low Cr) needed then corrosion resistance of bulk [illegible] - coatings needed

ZrO_2 coated [illegible] (need 100μ thick)

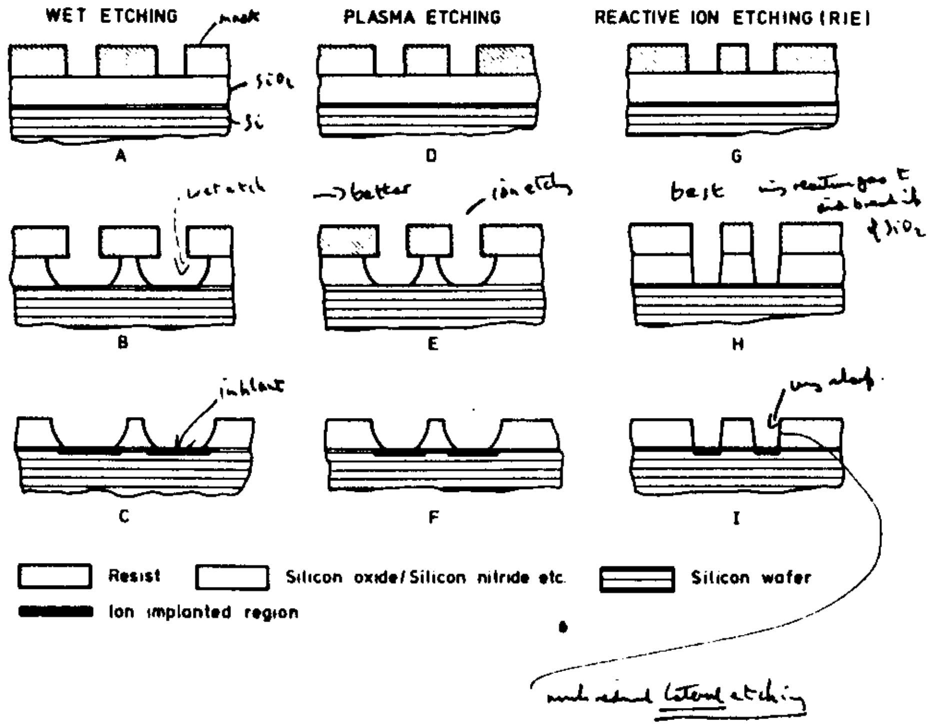
Advanced alloys are deposited to inhibit oxydation and corrosion.

LECTURE 1 : SLIDE 37

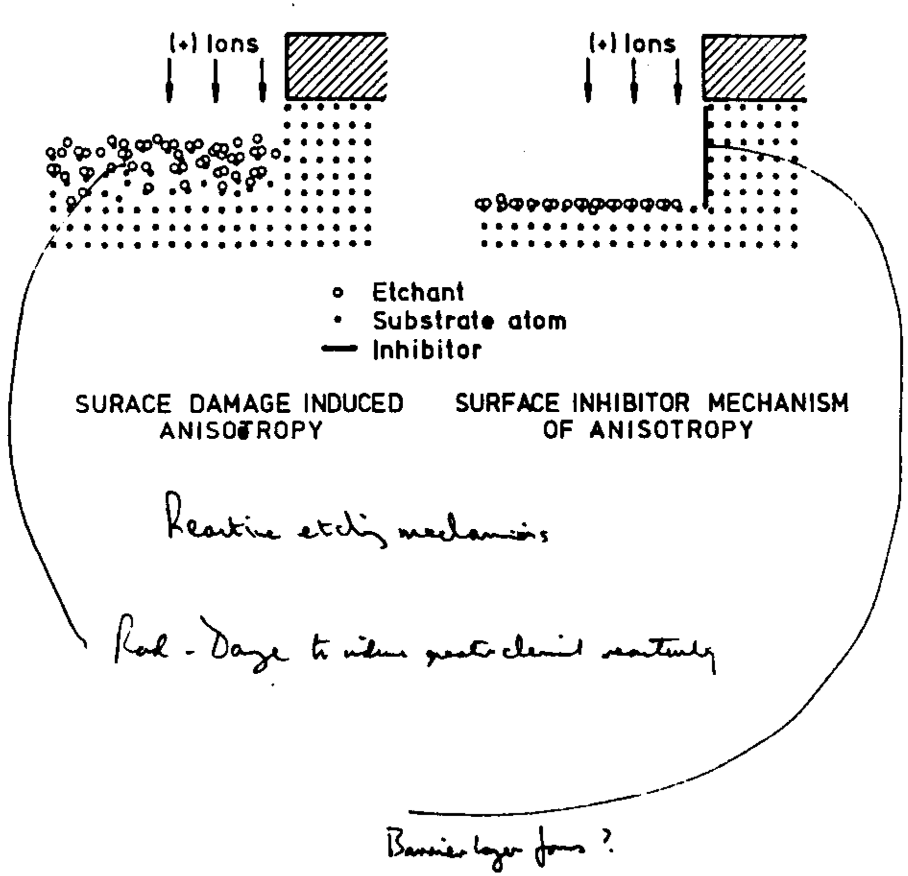
OPTICAL [illegible]
OF AN ADVANCED
[illegible] [illegible] DESIGNED
AT HARWELL

Masking used

LECTURE 1 : SLIDE 38



LECTURE 1 : SLIDE ~~40~~ 39



SUMMARY

A. PLASMA PROCESSING IS VERY VERSATILE AND COVERS A WIDE RANGE OF INDUSTRIES

B. PLASMAS CAN BE USED AS HEAT SOURCES, CHEMICAL SOURCES AND SOURCES OF SPECIES FOR EROSION/ SPUTTERING

C. ATTENTION TO THE DETAILS OF PLASMAS IS IMPORTANT