1. Introduction

1.1. General

Each material surface is exposed to various environmental influences. The surface of a solid body is sbujected to corrosion and wear and interacts with light and electromagnetc fields. From the technological point of view the miniaturization of mechanic, electronic, optical and optoelectronic components permanently increases the surface to volume ratio of the involved materials. In modern material science specific surface properties therefore gain increasing importance.

Nonetheless, the desired mechanical, optical chemical or electronic properties are often opposed to the bulk properties which may be high mechanical stability, easy manufacturing or low material cost. Because of this fact a multitude if High Tech components are composite materials which means that the surface properties significantly differ from the bulk properties. An example may be a mechanical part which has to exhibit high hardness (i. e. low wear under tribological load) as well as high fracture toughness (i. e. high resiestance against crack propagation). One material alone may not fulfill these demands. The solution of the problem can be a composite material consisting of a surface zone (coating) with high surface hardness and a tough bulk core.

Other machine components as e. g. high temperature blades of gas turbines have to exhibit high temperature and corrosion resistance as well as high mechanical stability. Also in this case one property such as corrosion resistance can be provided by a modified surface or a coating while mechanical stability is given by the base material.

Another large filed of examples is constituted by thin film systems which act as laser mirrors, anti reflex coatings and other optically active surface modifications. In the optical industry they are deposited on substrates which guarantee mechanical stability and other specific properties. Thin films can also be found in optoelectronic, electronic and magnetic components which can only be manufactured because of the special physical properties of thin films which may deviate significantly from those of the bulk material. A prominent example foe this case are hard disk read heads based on the Giant Magnetoresistance effect (GMR) which only operate due to the special properies of a combination of magnetic and insulating thin films.

1.2. History

In the following a brief history of thin film technology is given for the sake of completeness:

~1650: Observation and interpretation of interference patterns (e. g. oil on water) by R.Boyle, R.Hooke, I.Newton.

~1850: Development of first deposition techniques (M.Faraday; W.Grove; T.A.Edison) and of methods of thickness determination (Arago, Fizeau; Wernicke; Wiener) Commercial introduction of electrochemistry (Galvanics) for gold plating of uniform-accessoires.

~1940: Industrial manufacturing of coatings for optical, electronical and mechanical applications (mostly military).

~1965: Thin film technology develops to an integral part of the mass manufacturing processes in semiconductor and optical industry.

~1990: Thin films of High Tc-Superconductors.

~1995: Thin film processing allows for the tailoring of microstructures of atomic and mesoscopic dimensions („Quantum-Dots“ by PVD, „Cu-technology“ by electrochemistry applied to integrated circuits).

~2000: Manufacturing of nanocrystalline materials with defined composition and structure for applications as protective coatings and in tribology. Deposition of highly ordered two and three dimensional objects with sizes in the nm range.

~2004: Upscaling of complex reactive coating processes for industrial applications (coatings on glass, thermal management). Combinatorial investigation of ternery and quartenery material systems.

~2006: Investigation of organic coatings leads to the emergence of organic electronics (OLED, printable circuits).

~2010: Preparation and characterization of the prototype two dimensional (2d) material, Graphene. Introduction of reliable solid state touch screens to communication media (Smartphone).

~2015: Generation of heterostructures made from 2d materials. Approaches to manufacture flexible electronic devices consisting of ultrathin materials.

1.3. Definition of Terms

In the beginning the following definitions may be useful:

Substrate:

Base material on of a film; (there may be, however, also free standing films!)

Film, Coating:

Solid (or liquid) body which exhibits a significantly lower geometrical extension in one dimension then in the remaining two spatial dimensions. The properties of the film or coating have to differ significantly from the bulk.

Distinction: "Thin" Film - "Thick" Film:

The limit between "thin" and "thick" films cannot generally be defined, although literature sometimes gives an arbitrary value of 1 µm. Basically, a film can be considered as "thin" when ist properties are significantly different from the bulk. This can be due to:

1. the increasing surface to volume ratio at decreasing film thickness,

and

2. the microscopic structure which is dependent on the deposition parameters

ad **1**.: a low film thickness can cause the following effects : optical interferences, increase of the electrical resistivity and decrease of the temperature coefficient of electrical resistivity, increase of the critical magnetic induction and of the critical temperature in superconducrivity, tunnelling of Cooper pairs (Josephson-effect). The film thicknesses which lead to the appearance of these thin film effects can be quite different. An Indium-Oxide film (In_2O_3), e. g., which can be used as temperature barrier coating due to its high transmission in the visible region and its high reflectivity in the infrared region (this is caused by optical interference effects) has to be approx. 300 nm thick. For optical applications this film can be considered as thin. If the same material would serve as insulator in a Josephson junction, 300 nm would be much to thick to allow Cooper pairs to tunnel through the oxide. For this application the In_2O_3 film should have a thickness of only 2 nm. In other words: for one given application a film can be considered as "thin" while for another one the film can still be considered as "thick".

ad **2**.: as a consequence of a microstructure which is different from the bulk (e. g. in respect to grain or crystallite size) the following effects may be observed: increase of corrosion resistance, increase of hardness, increase of the magnetic saturation induction, increase of the critical temperature of superconductivity, increase of the optical absorption. Structures like this are often metastable and can not only be achieved by thin film deposition methods, but also by many different methods of surface modification as there are electron beam, laser surface melting or ion implantation. In the latter case the "thin film" is a modified surface zone with properties significantly different from the bulk. Also in this case thicknesses range from few nm to severel µm, and no definite distinction between "thin" and "thick" coatings may be justified.

Surface and Interface:

In general, each border between well discernible phases is termed as "Interface". This can be the interface between a substrate and a film or between a coating and the environment, but also e. g. a grain boundary between two single crystalline grains in a solid. The term "Surface" is a sub quantity of the term "Interface" and designates the border between a solid or a liquid and gas or vacuum.

Film Deposition and Film Formation

The deposition process of a film can be devided into three basic phases:

1. Preparation of the film forming particles (atoms, molecules, cluster)

2. Transport of the particles from the source to the substrate

3. Adsorption of the particles on the substrate and film growth

These phases can - depending on the specific deposition process and/or on the choice of the deposition parameters - be considered as either independent or as influencing one another. The former is desirable since it allows to control the basic steps independently and therefore yields a high flexibility in the deposition process.

1.4. Applications of Thin Film Technology

Engineering/Processing

... Tribological Applications: Protective coatings to reduce wear, corrosion and erosion, low lriction coatings

... Hard coatings for cutting tools

... Surface passivation

... Protection afainst high temperature corrosion

... Self-supporting coatings of refractory metals for rocket nozzles, crucibles, pipes

... Decorative coatings

... Catalysing coatings

Optics

... Antireflex coatings ("Multicoated Optics")

... Highly reflecting coatings (laser mirrors)

... Interference filters

... Beam splitter and thin film polarizers

... Integrated optics

Optoelectronics

... Photodetectors

... Image transmission

... Optical memories

... LCD/TFT

Electronics

... Passive thin film elements (Resistors, Condensers, Interconnects)

... Active thin film elements (Transistors, Diodes)

... Integrierted Circuits (VLSI, Very Large Scale Integrated Circuit)

... CCD (Charge Coupled Device)

Cryotechnics

... Superconducting thin films, switches, memories

... SQUIDS (Superconducting Quantum Interference Devices)

New Materials

... Superhard carbon ("Diamond")

... Amorphous silicon

... Metastable phases: Metallic glasses

... Ultrafine powders (diameter < 10nm)

... Spheroidization of high melting point materials (diameter 1-500µm)

... High purity smiconductors (GaAs)

(Alternative) Energies

... Solar collectors and solar cells

... Thermal management of erchitectural glasses and foils

... Thermal insulation (metal coated foils)

Magnetic Applicaions

... Audio, video and computer memories

... Magnetic read/write heads

Sensorics

... Data acquisition in argessive environments and media

... Telemetry

... Biological Sensorics

Biomedicine

... Biocompatible implant coatings

... Neurological sensors

... Claddings for depot pharmaca

1.5. Deposition Methods - Overview

PVD (Physical Vapour Deposition)

- Evaporation

- Sputtering
  - Diode-system
  - Triode-system
  - Magnetron-system ("balanced/unbalanced")
  - Ion beam-system

- Ionplating
  - DC-glow-discharge
  - RF-glow-discharge
  - Magnetron- discharge
  - Arc-discharge
  - Ion-Cluster-beam

- Reactive versions of the above processes

CVD (Chemical Vapour Deposition)
- Thermal CVD
- Plasma-activated CVD
- Photon- activated CVD
- Laser-induced CVD

Plasmapolymerization

Electrochemical deposition
- Cathodic deposition
- Anodic oxidation
- Elektrophoresis
- Chemical deposition

Thermal Spraying
- Flame
- Explosion
- Arc
- Plasma

Electro-Surfacing
- Flame
- Arc
- Plasma
- Laser

Plating
- Casting
- Rolling
- Explosion
- Rubbing

Deposition from the Melt

Deposition from Emulsions, Pastes
- Mechanic
- Thermal
- Spray

1.6. Film Thickness and Deposition Rates

With the deposition methods described above a region in film thickness can be covered which reaches from less than 1 nm to several 10 mm. These are 6 to 7 orders of magnitude! The regions given in Fig. 1.1. and 1.2. are average values for films of good quality which can be deposited in reasonable times.

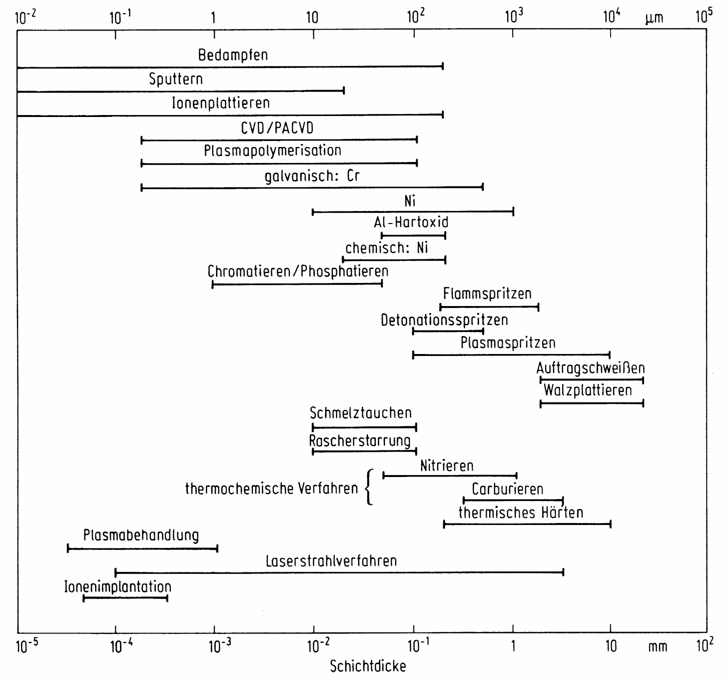

Fig. 1.1.: Film Thicknesses achievable by several deposition methods [1, p. 10]

From Fig 1.1. and 1.2. it is also visible thet methods based on spraying, plating and welding yield much higher thickness and rate than PVD, CVD or (electro)chemical methods.

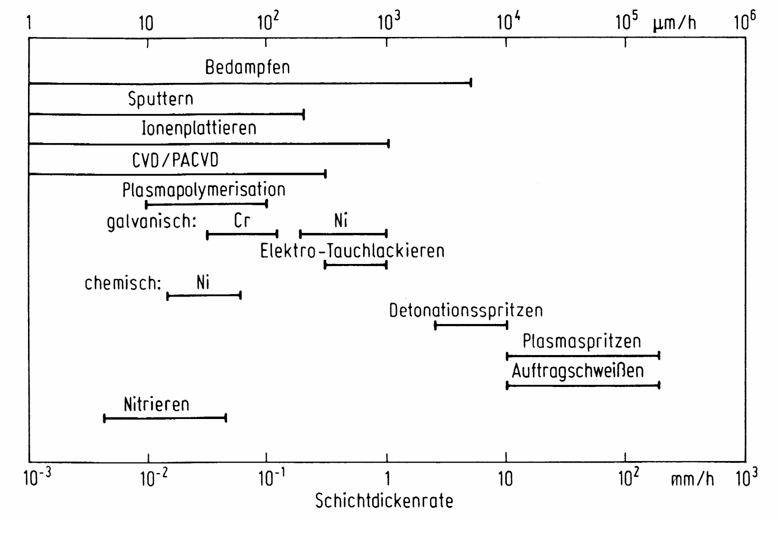

Abb. 1.2.: Deposition rates achievable by several deposition methods [1, p. 11]