Surface Engineering and Coatings

Ali Erdemir
Argonne National Laboratory
Energy Technology Division
Tribology Section
Argonne, IL 60439

Ivan Petrov
Center for Microanalysis of Materials
Frederick Seitz Materials Research Laboratory
University of Illinois
104 S. Goodwin Avenue
Urbana, IL 61801

Lecture 1
Course Outline

- Mon 8:30-12:00
  - L1: Introduction to Surface Engineering and Coating Processes (PVD, CVD, Ion-Beam and Other Techniques)
  - L3: Fundamentals of Sputter Deposition
- Mon 1:00-4:30 pm
  - L4: Fundamentals of Nucleation and Growth
  - L5: Computational Methods: Atomistic and Molecular Dynamics Simulation of Film Growth
  - P1: Lab tour: Thin film deposition and surface engineering facilities (MSE)
- Tue 8:30-12:00
  - L6: Recent Advances in Surface Cleaning and Preparation Techniques
  - L7: Recent Advances in Surface Engineering and Coating Technologies
  - L8: Hybrid Coatings and Deposition Processes
- Tue 1:00-4:30 pm
  - L9: Novel Coating Architectures (Nano-structured and -composite films, superlattice, compositionally/structurally modulated systems, hybridization of coatings with surface texturing and/or patterning)
  - L10: Scale-up and Design; Industrial Systems and Practices
  - P2: Hands-on with Plasma Deposition Processes
Outline Cont’d

- Wed 8:30-12:00
  - L11: Introduction to Thin Film Characterization
  - L12: Surface Characterization (physical and chemical methods, XPS, AES, SIMS, etc)
  - L13: Structural Characterization (TEM, SEM, etc.)
- Wed 1:00-4:30 pm
  - L14: Mechanical Characterization (Adhesion, Hardness, Elastic Properties, Toughness, etc.)
  - P3: Lab Tour: Surface and Structural Characterization Facilities
  - P4: Practical Experience with Some of the Characterization Methods (SEM, TEM, AFM, etc.)
- Thu 8:30-12:00
  - L15: Tribological Characterization
  - L15: An Overview of Emerging Technologies
  - L16: Superhardness and superlubricity: theory and experiments
- Thu 1:00-4:30 pm
  - L17: Classification and Industrial Applications of Coatings
  - P4: Lab Tour: Tribology Test Facilities (ME)
  - P5: Hands-on Nano-indentation, Tribology
Outline Cont’d

• Fri 8:30-12:00

  - L18: Guest Speaker 1: Dr. K. Wahl, NRL
    Nanomechanics and tribology of coatings

  - L19: Guest Speaker 2: Prof. Y.-W. Chung, NSF.
    Applications of Tribological Coatings in Extremely High-Density Computer Disk Drive Applications

  - L20: Guest Speaker: Dr. Jeffrey Sanders, AFRL/MLBT
    Advanced Materials and Coatings for Aerospace Applications

• Tentative Lab Tours

  - Material Science & Engineering
  - Mechanical Engineering
  - NUANCE Microscopy Facility
  - Surface Electron & X-Ray Diffraction
L1: INTRODUCTION TO SURFACE ENGINEERING AND COATING PROCESSES
**Surface Engineering**

- **Definition:** Modification of near-surface structure, chemistry or property of a substrate in order to achieve superior performance and/or durability. It is an enabling technology and can impact a wide range of industrial sectors.
  - Combining chemistry, physics, and mechanical engineering with metallurgy and materials science, it contributes to virtually all engineering disciplines.
  - It can be done on a given surface by metallurgical, mechanical, physical, and chemical means, or by producing a thick layer or a thin coating.
  - Both metallic and non-metallic surfaces can be engineered to provide improved property or performance.

Examples of Surface Engineering Processes

- Textured
- Nitrided
- Coated

Examples of Engineered Surfaces

- Multilayer Coatings
- Plasma Spray Coating
What are the benefits and where are they used?

- Specific properties rely on surfaces
  - Wear, friction, corrosion, fatigue, reflectivity, emissivity, color, thermal/electrical conductivity, bio-compatibility, etc.
- Benefits
  - Extend product life (durability)
  - Improve resistance to wear, oxidation and corrosion (performance)
  - Satisfy the consumer's need for better and lower cost components
  - Reduce maintenance (reliability and cost)
  - Reduce emissions and environmental waste
  - Improve the appearance; visually attractiveness
  - Improve electrical conductivity
  - Improve solderability
  - Metallize plastic component surfaces
  - Provide shielding for electromagnetic and radio frequency radiation.
- By improving durability, it reduces waste of natural resources and energy.
- Surface engineered automotive parts and components can extend warranties and reduce emissions. For example: A hardened engine valve will last a minimum of five years without replacement.
Scales of Surface Engineering

- Surface engineering technologies span:
  - Five orders of magnitude in thickness
    - It can vary from several mm for weld overlays to a few atomic layers or nanometers for physical vapor deposition (PVD) and chemical vapor deposition (CVD) coatings or ion implantation. Atomic-layer deposition is also possible.
  - Three orders of magnitude in hardness
    - Example of coating hardness range from 250-300 Hv for soft metal or spray coatings, 3500 Hv for Titanium Nitride PVD coatings and up to 10,000 Hv for diamond coatings
  - Almost infinite possibilities in the range of compositions and/or microstructure
    - Nano-composite, nano-layered, amorphous, crystalline, quasi-crystalline, etc.
Evolution and Significance of Surface Engineering

- It is an enabling technology
- It can combine various surface treatments with thin film and coating deposition.
- It can substantially improve wear and corrosion resistance of structural components.
- It increases component lifetime and resistance to aggressive environments.
- It can produce functional coatings that modify biocompatibility and optical and electrical properties of critical components.

Evolution of Coating Architectures

Single component (1980s)

Multicomponent, Multilayer (1990s)

Nanostructured, Superlattice, Gradient

(2000 and beyond)

Adaptative (smart)
Classification of Surface Engineering Processes

- The traditional, well established processes:
  - Painting
  - Electroplating
  - Galvanizing
  - Thermal and plasma spraying
  - Nitriding, Carburizing, Boriding

- The more technologically advanced coating technologies:
  - Physical and chemical vapor deposition
  - Ion implantation
  - Ion-assisted deposition
  - Ion-beam mixing
  - Laser treatment

- Nowadays, a multitude of options are available to select and specify a treatment or a combination of treatments to engineer the surfaces of components or structures.
Classification of Various Coating Methods

SURFACE COATING METHODS

Gaseous State
- CVD
- PVD
- IBAD
- Plasma variants

Solution State
- Chemical solution deposition
- Electrochemical deposition
- Sol gel
- Laser
- Thermal spraying

Molten or semi-molten State
- Chemical reduction
- Electroless deposition
- Chemical conversion
- Plasma variants

Major Emphasis of This Course

Physical Vapor Deposition (PVD)
Chemical Vapor Deposition (CVD)

- Are special methods by which a protective hard or soft film can be produced
  - Preferably on the outer surfaces of a machine element
  - Desired results: superior performance, protection, durability.

Various engine parts treated by PVD

Multilayer CVD coatings

Gear systems

Cutting and forming tools²
CVD and PVD: Enabling Surface Technologies

- CVD/PVD can effectively modify near-surface structure and/or chemistry of mechanical parts or components and hence improve their performance and increase their durability/reliability.
- As enabling technologies, they can impact a wide range of industrial sectors.
- Both metallic and non-metallic surfaces can be engineered by CVD and PVD.
MODERN PRACTICES IN PVD AND CVD

One Process
One System
Many Coating Solutions

PACVD
ARC-PVD

Make Your Choice

TIN
TiAlN
TiCN
TiN

TIN
TINALOX™
ALOX™

MoS₂
DLC
B₄C
CBN
CrN

MultiLayer

TIAM

TIN
TiB₂

DLC
MoS₂
B₄C

Make Your Choice

Copyright of CemeCon, GMBH
Large-scale Systems

In-line PVD

Sputtering

Arc-PVD

CVD
Physical Vapor Deposition (PVD)

- PVD: A type of vacuum deposition process where a material is vaporized in a vacuum chamber, transported atom by atom across the chamber to the substrate, and condensed into a film at the substrate's surface.

It provides the kind of super-critical, non-equilibrium chemical/physical states needed for the synthesis of new coatings with unusual properties, such as super-hardness or low friction.
Classification of PVD

Physical Vapor Deposition (PVD)

Evaporative PVD
- Resistive
- Inductive
- Electron Beam Gun
- Arc
- Laser

Sputtering PVD
- Diode
- Magnetron
- Ion Beam
- Triode

Examples of Plasma-based PVD Processes

 Ion plating  Activated reactive evaporation  Cathodic arc deposition

 Bias sputter deposition  Ion-beam assisted deposition  Dual ion-beam sputtering
Evaporative PVD Processes

- EB Evaporation PVD
- Thermal Evaporation PVD
- Laser Evaporation or Ablation
Sputter Deposition

Basics:
- A voltage is applied across a rarified gas.
- Breakdown of the gas forms a glow discharge plasma.
- Positive ions from the plasma strike the negative electrode.
- Energy from the ions is transferred to target atoms.
- A few of these may escape from the target surface (they are sputtered).
- The sputtered atoms condense on the substrate forming a film.

Magnetron: a device in which a magnet system on the back of the cathode deflects the electrons, thus lengthening the ionization path. The accelerated ions transfer their momentum to particles of the coating material, which are then deposited on the substrate.
Various Sputtering Methods

- Cold Cathode DC Diode sputtering
- DC triode Sputtering
- AC Sputtering
- Rf Sputtering
- DC Magnetron Sputtering
  - Unbalanced Magnetron
  - Balanced Magnetron
  - Pulsed DC Magnetron
  - Ion and Plasma Beam Sputtering

Schematic representation

Ion-beam sputtering
Sputtering Mechanism

- Bombardment of solid (target) by high energy chemically inert ions (e.g. Ar+) that are extracted from plasma.
- Such bombardment causes ejection of atoms from the target which are then re-deposited on the surface of the substrate purposely located in the vicinity of the target.
Diode vs Magnetron Sputtering

**Diode**

- **Comments:**
  - Simple, relative ease in fabrication and thickness uniformity over large area
  - Relatively high deposition pressure and relatively high substrate temperature

**Magnetron**

- **Comments:**
  - High deposition rates, low deposition pressure, low substrate temperature, can be scaled up, so commonly used for industrial production
  - More complex than planar diode systems
Ion Beam Sputtering

A physical vapor deposition process in which the coating material (target) is removed from the surface of the coating source (cathode) by a flux of high energy ions and deposited upon the surface of substrates.

It can also be used to sputter-off or clean substrate surface.
ARC PVD

- Main Characteristics
  - High Vaporization Rate
  - High Ionization Rate
  - High Throughputs
  - High Deposition Rate
  - Strong film/substrate bonding

Micro/macro-droplets
May cause problems
**PVD, CVD Systems**

Nitride coatings (TiN, CrN, ZrN)
Carbide and Carbonitride coatings (TiC, TiCN)
Multicomponent Coatings (TiAlN)
DLC and Diamond Coatings etc.
Thickness: 1 to 100 microns
Operating Temperature: RT to 500-600°C
FILTERED ARC

• The filtered cathodic arc may be used to produce a range coatings
• It reduce/eliminate microdroplets associated with conventional arc evaporation
• High deposition rates are available for most materials and compounds
• It does not promote/cause poisoning of the cathodes in reactive deposition
• It provides very ionization
• It is cheaper than electron beam methods
• It is suitable for most metals including high temperature materials (Ta, W, C)
  • It cannot be used for evaporating semi-/ or di-electric materials
  • It cannot be used for evaporating low heat conductivity materials
It is a vacuum-deposition process that combines physical vapor deposition (PVD) with ion-beam bombardment. A vapor of coating atoms is generated with an electron-beam evaporator and deposited on a substrate. Ions, typically gaseous, are simultaneously extracted from a plasma and accelerated into the growing PVD film at energies of several hundred to several thousand electronvolts (eV).

- Good for high-value added applications or science
- Difficulty in scaling-up
Chemical Vapor Deposition (CVD)

- **CVD** is a process in which the gaseous species are transported to the reaction chamber, activated thermally or by a plasma in the vicinity of the substrate, and made to react to form a solid deposit on the substrate surface (R. F. Bunshah)
- CVD is a relatively mature technique
- Used in electronic, optoelectronic, tooling industry, ceramic fiber production etc,

- It is possible to deposit films of uniform thickness and low porosity even on substrates of complicated shape in CVD.
Classification of CVD

Chemical Vapour Deposition (CVD)

- Chemical Vapor Infiltration
  - Metal - Organic
    - Metal – Organic Vapor Phase Epitaxy
- Hot Filament
- Laser Assisted
- Electron Assisted
  - Low Pressure
- Plasma Assisted
  - Atomic Layer Epitaxy
  - DC Plasma
  - Pulse Plasma
  - AC Plasma
  - rf Plasma
  - Microwave Plasma

The Gas-Phase Chemistry of CVD Processes

- **Thermal-Decomposition Reactions:**
  - Hydrocarbon Decomposition: \( \text{CH}_4(g) \rightarrow \text{C(s)}+2\text{H}_2(g) \)
  - Halide Decomposition: \( \text{WF}_6(g) \rightarrow \text{W(s)}+3\text{F}_6(g) \)
  - Carbonyl Decomposition: \( \text{Ni(CO)}_4(g) \rightarrow \text{Ni(s)}+4\text{CO(g)} \)
  - Hydride Decomposition: \( \text{SiH}_4(g) \rightarrow \text{Si(s)}+2\text{H}_2(g) \)

- **Hydrogen Reduction:**
  \( \text{SiCl}_4(g)+2\text{H}_2(g) \rightarrow \text{Si(s)}+4\text{HCl(g)} \)

- **Co-reduction:**
  \( \text{TiCl}_4(g)+2\text{BCl}_3(g)+5\text{H}_2(g) \rightarrow \text{TiB}_2(s)+10\text{HCl(g)} \)

- **Reactions Leading to Carbide and Nitride Formation:**
  \( \text{TiCl}_4(g)+\text{CH}_4(g) \rightarrow \text{TiC(s)}+4\text{HCl(g)} \)
  \( 3\text{SiCl}_4(g)+4\text{NH}_3(g) \rightarrow \text{Si}_3\text{N}_4(s)+12\text{HCl(g)} \)

CVD is able to produce single or multilayer coatings with composite or nanostructured architectures. It is not a line of sight process, hence allows the coating of complex shaped engineering components. Major drawbacks: Safety issue (hazardous, flammable gases), high-temperature requirement.
Example of Plasma Assisted CVD

Plasma-enhanced CVD

Hot-filament CVD

Chemical/Physical Events That Control Nucleation and Growth

Used in Deposition Of DLC

Reagents

$\text{H}_2 + \text{CH}_4$

Activation

$\bullet \text{C} + \text{Heat}$

$\text{H}_2 \rightarrow 2\text{H} \bullet$

$\text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2$

Transport and reaction
Future Directions in PVD and CVD Processes

1980s 1900s 2000s

- Single component
- Multicomponent, Multilayer
- Nanostructured, Superlattice, Gradient
- Textured, Adaptive (smart)

Smart Processes (hybrids, etc.)

Novel Coating Architectures for the 21st Century

- Nano-composite coatings
- Sculptured Coatings
- Superlattice and/or multi-layer coatings
Key References