Roadmap for Functional Coatings and Surface Modification

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Functional coatings and surface modifications revolutionized the whole industry. Examples are: hard face coating of tools, coatings for energy conversion, plating for electronics circuits, surface modification for microelectronic, reflective and absorptive deposits for optics, bio-compatible interfaces, nano-materials and more.

The production of functional films and surfaces has technological and economical advantages to the coating and finishing industries.

A roadmap was drawn for functional films and surface technologies, for the short and long-term years. The work analyses the demands for performance and products and analyses need for functional coatings and surfaces.

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Introduction.

The surface technology has become the most influential technology in the development of the high-tech hardware. Most of the performance achievements and the innovation accomplishment in the high-tech industries are due to functional coatings. Thus includes advanced cutting tools with hard coatings, micro electronics and micro-optical devices which are produced by surface technologies, satellite energy conversion or photovoltaic energy source are based on functional coating, bio-chips, magnetic storage and so forth. Moreover, the competitiveness and potential growth of companies is directly related to the quality and new functionality of coatings and films. This modern time was referred to as "The Era of Functional Coating" (Interfinish 1986, Paris).

There are many application areas in which functional surface and films play strategic role. The discussion of this paper focuses around the following selected application areas.

- Optical applications
- Tribological applications
- Micro-electronics
- Bio-Medical application.

All those application areas are technology driven by functional surfaces. Many of the contemporary, and most of the envisaged advanced applications in those areas would be based on development in surface and coating technologies. Therefore, the roadmapping of those technologies is essential for the improvement of the performances and the development of new and innovative products in those application areas.

Optical Application:

Optical coating:

Functional coated surfaces is utilized in most of the optical devices, such as lenses, cameras, compact discs and players, up to the high end devices including optical systems in fundamental research. The more the criticality of the function of the coating, there raised the need for knowledge-based process. In many cases the function of the device or its efficiency depends on the relevant functional coating. As a consequence, optical coatings are considered as one of the major enabling technologies for a broad spectrum of application and future developments.

Vacuum deposition processes today deposit most optical coatings. Machines for deposition range from enormous machines for coating architectural glass to small batch coaters for spectacle lenses and laser mirrors. Coatings range in complexity from one or two layers to several hundred.

Optoelectronic components

For core network components, the drive will be for higher data rates. The increase is reached through higher bit-rate per wavelength: 2.5 to 10 to 40Gbit/s and further, or through an increasing number of wavelengths per channel. This requires optical band extension, improved transmission fibers, higher speed optoelectronic devices and specific microelectronic functions, and higher integration of components. With increasing data rates on the optical path, the incentive is for increasing number of functions to be implemented on the optical stream without conversion to electronic signals. Integrated optics on appropriate substrate material aims to achieve optimal data rate. On-going improvement of data rage is achieved by enhancing optical layer materials, introduction of new multi-layers and other thin film technology optical devices. Optical amplification is commonly achieved using Erbium doped fibers, and emerging low noise alternatives include Raman amplification.

The Optical Thin Films advanced applications:

In order to get desired optical properties from a thin film, complex chemistries and production methods must be employed. The major challenge in the development of optical thin films is to find the correct chemistry, which generates the desired optical properties and to be able to produce it in a high volume environment with high quality and cost effectiveness.

Light sources:

Laser diodes and light emitting diodes are made of multilayers and produced by various surface technologies.

Solid-state lasers, complement diode lasers by offering better spatial beam profile properties and a very broad spectral range from the mid ultra-violet to the mid-infrared needed for applications in information technology, sensors, and environmental monitoring. They are expected to totally replace gas lasers and dye lasers in the coming few years, offering more reliable consumer friendly operation in more compact units with equally good beam quality.

Organic Light Emitting Diode (OLED)

Organic Light Emitting Diodes are candidate to replace existing light sources and panels. If new approaches such as OLED are to succeed, it is essential that proponents work together to identify and remove the barriers to improved performance and commercialization. It will also be necessary to match the technological developments to the requirements of specific market opportunities.

Recent advances in the development of organic materials to conduct electricity and emit light should provide the basis for the economic manufacture of active matrix displays built upon organic light emitting diode (OLED) technology. The steps leading from laboratory science and prototype demonstrations to high-volume low-cost fabrication in the coming years have been outlined and the major processing challenges identified.

Materials for nonlinear optics and light detection

In a broad sense, nonlinear optics includes all effects whereby an electromagnetic field affects the propagation of another electromagnetic field. This usually occurs through modulation by the control field of the refractive index "seen" by the probe field, thus affecting beam propagation phenomena such as convergence, diffraction, or absorption.

Semiconductors Heterostructures and in general bandgap engineering has been essential for the fast modulation and detection of light over an extended spectral bandwidth. Present challenges include the bandwidth extension beyond 40 Gbits/s per channel and direct microwave modulation optical signals.

Passive optical film materials

Optical materials are "synthetic" materials, as they require sophisticated elaboration processes. *Mesoscopic patterning of optical materials* in addition combine mesoscopic structures smaller than the optical wavelength that confers optical properties different from the bulk and strongly dependent on detailed microstructure. The simplest case is thin film deposition for reflection control, where loss control down to less than one part in a million is still a challenge, for example for high accuracy interferometry and for high power laser applications. Multilayers providing high reflection in the extreme ultraviolet domain are a challenge for year 2008 nanolithography with a significant impact on the microelectronics market. 2D and 3D microstructures give rise to the "photonic bandgap materials", that offer a very nice combination of basic science research opportunities and very large application potential for the fabrication of highly integrated photonic circuits, firstly in a planar guided wave configuration and in the longer term perhaps in 3D space.

Tribological and Mechanical Applications

Tribology deals with friction, wear and lubrication. It has developed from simple mean value predictions towards atomic level understanding. The phenomena seen at dry contacts and thin film lubrication contacts have now reached the micro-to nanometer level. Friction and wear cannot be predicted using continuum mechanics when the phenomena studied take place within a few atom layers. Current techniques enable the measurement of tribological properties at the micro- and nano-scale. This is a truly multidisciplinary endeavor, making use of molecular dynamic computer simulations and atomic force microscopy applicable in numerous problems of physics, (bio-)chemistry and micro- and nano-mechanical engineering. These new developments are dramatically changing our basic understanding of the phenomena that govern friction and wear processes. Micro- and nanotribology may therefore lead to breakthrough results defining the regimes for ultra-low friction and near zero wear.

Tribology will have a major impact on the economy as well as on our daily lives. To give just a few examples:

- The combination of bio-functionality with inorganic materials needed for instance for medical prostheses and leading to a huge improvement in quality of life and reduction in health care cost.
- Nanostructured materials provide new opportunities for lightweight, long-lived, yet strong components: strength for function and safety, low weight for energy economy and agility, and low failure rates (wear, corrosion, fracture and fatigue) for life-cycle cost and

waste reduction. Nanostructured coatings will lead to long lasting, self-cleaning surface finishes, reducing friction, wear and corrosion.

• Microelectromechanical systems, or MEMS, are now revolutionising the automotive, optical, printing and medical industries. Typical applications include miniature sensors, actuators, and control systems, microfluid systems, systems for drug delivery and microsurgery, microprostheses, gene chips (BIOMEMS). The life span and reliability of these microsystems are of prime importance. Because the friction forces that are proportional to the surface, decrease a thousand times less than the inertial and electromagnetic forces that are proportional to the volume, tribological issues are critical.

• In nanoelectromechanical systems, or NEMS, critical feature sizes range from hundreds to only a few nanometres, where new physical properties dominate the operation of the devices. NEMS are patterned at the nanoscale, which makes them capable to interface with molecular systems, combining the power of biotechnology with engineered devices. Carbon nanotubes are being widely explored for their functioning in NEMS. NEMS technology will create a revolutionary new class of devices including highly functional (bio)sensors, non-invasive medical diagnostic tools, and ultra-high density data storage devices.

• Micro- and nanostructured tribomaterials

Novel material technologies, e.g. hybrid PVD + plasma assisted CVD surface treatments, allow for the design of completely new materials by combining materials available today only by using completely different processes.

Functionally graded coating.

An innovative approach to tribological coating is the functionally graded hard coating. Such functional graded coating can be achieved either by graded change of film composition during the coating process of by changing film properties at the same way. Such a coating needs a process that the compositions of layer properties are controllable throughout the process. Such procedures could be the deposition by magnetron sputtering or reactive sputtering, while controlling the deposition process.

DLC (diamond Like Coating)

DLC coatings of varying composition are deposited in many different processes. In magnetic storage technology, e.g. hard disks, a-C:H films are used to protect the magnetic layers against damage by a touching head and their impact will increase in the near future. Modifications, for example, by adding nitrogen to the a-C:H matrix in the protective overcoat of magnetic thin film rigid disks resulted in improved performance (wear, start/stop cycles, stiction) compared to pure a-C:H. Incorporation of fluorine changes the surface energy of the a-C:H, to prevent stiction of the read/write head in magnetic rigid disks without loosing the wear resistance. A similar application for DLC coatings is as protections for VCR head drums against wear from the tape by dust and embedded Fe oxide particles. In the automotive industry, numerous parts coated with DLC have already been investigated, for example transmission gears. Also, gears coated with WC/C have shown an increased lifetime under loss-of-lubrication. The real extent of usage in automotive industry is kept confidential but some parts today are coated in the production-line

with DLC, as for example rollers, piston rings, cylinders, valve guides and stems, and fuel injectors.

Hardmetal Thermal Sprayed Coating

Thermal spray processes (e.g. atmospheric plasma spraying (APS), vacuum plasma spraying (VPS), high velocity oxy-fuel (HVOF) spraying as the most important processes), represent an important and rapidly growing group of surface modification technologies to produce hardmetal coatings for protection against wear and corrosion. This type of coatings with a typical thickness in the range of 100-400 μ m is used in nearly all industrial areas and discovers permanently new applications. It is also a competing technology to several other surface modification technologies, e.g. the replacement of hard chromium coatings by HVOF sprayed coatings is under intensive discussion.

CVD and PVD hard Coatings.

PVD and CVD technologies play an important role in tool hard coating.

The basic and widely use is the coating of TiN made by sputtering and other PVD processes. However, other hard CVD and PVD coatings are used for various objectives.

Diamond coating is used as anti-scratch coating. It is used for missiles' windows coating. While protecting those windows from the environment, it has no adverse impact on light transmission.

Ball bearings are using advanced sputtering coating of MoS_2 entrapped in TiN. It is applied on systems that operate in remote places, where regular maintenance and lubrication is not performed. Some tools are coated with minutes of MoS_2 incorporated in TiN. Those minute amounts are enough to increase the service life of those tools.

While cutting tool requires hard coat with low thermal conductivity, drilling tool requires high conductivity. For drilling tool the preferred coat is of Tungsten Carbide.

Easy- and self- cleaning surfaces

Other aspect of tribological coating is the easy cleaning and self-cleaning surfaces. Much effort is invested to develop such films and their production technologies.

Dry Lubrication.

Advances in dry lubrication is achieved by coating the surface with certain formulation to achieve a higher performance and durable such lubrication. This is obtained by impregnation of lubricant into a specially designed film. In the past few years, inorganic fullerene-like (e.g., IF) supramolecules of WS₂ and MoS₂ with structures closely related to (nested) carbon fullerenes and nanotubes have been synthesized. It was established that IF possess lubricating properties superior to those of well-known layered materials (e.g., 2H platelets). By confining the IF nanoparticles inside a porous and densified solid matrix, their slow release to the metal surface is expected to alleviate both friction losses and wear, while assuring the mechanical integrity of the powder metal composite.

Microelectronics

The electronics industry owes its advancement to the surface technology. The first innovation is the PCB, printed circuit board that replaces the traditional wiring in electronics devices. The PCB is based on polymeric substrate, such as glass-reinforced epoxy; where the wiring is a coat or etched laminate of metal. The effort is to increase the density of the lines on the PCB, improve the solderability of the contacts and the production of multilayer PCB. This technology is valid today, and is going under continues development of materials, printing technologies, masking materials etc.

The computation and the computerized instrumentation lead to the use of microelectronics devices. Those devices are currently based on silicon substrate. Most of the components of microelectronics are based on surface technologies and films. Such are oxidation of surfaces, ion implantation, doping, vacuum deposition and other processes. Microelectronics is expected to double its performance and components density every 1.5 to 2 years (Moore's law). Efforts are being made to introduce new technologies, materials and components in order to achieve the high performance growth in micro- and opto electronics. On chip pitch size is expected to reach 22 nanometers in the long term, and atomic scale for components within the next years. See the following table. (Source: ITRS rev. 2002 and other roadmaps and forecasting documents).

Year of	2004	2005	2006	2007	2010	2013	2016
production DRAM	90	80	70	65	45	32	22
¹ / ₂ pitch, nm			-			-	

Forecasted feature size via year of production

While most of the processes for PCB are conventional, microelectronics utilizes mostly physical or chemical vapour processes. For example, conductive lines are either chemical deposition or electrochemical deposition of copper for PCB. Interconnects of the microelectronics chips were made by vacuum deposition of aluminum. However, recent developments in Interconnects technology discovered the advantages of electrodeposition technique for copper metallization for VLSI circuits. Electroplated Copper offers significant speed, power reliability and cost over the conventional aluminum technology. Copper is typically integrated with low-K interlevel dielectric that reduce lines and inter-line capacitance, hence, improve overall speed and power performances.

One of the objectives of microelectronics is to integrate systems on chips, SOC. This enables efficient systems on chips with known CMOS process. This year, it is expected to have MEMS systems and chemical sensors on chip. Later on, electro optical systems are due to be integrated on chip, and on 2006, it is expected to see electro-biological systems on chip. (source: ITRS rev. 2002).

Opto-electronics:

New research works show that utilization or wet processes, may better the opto-electronic properties of surfaces. Example of this is the dip coating processes of ITO (Indium-Tin-Oxide) transparent conducting films. Further studies of wet processes may lead to the development of other processes and products with superior properties at low cost for future applications.

As to single-electron devices, these will be based on semiconductor quantum dots (also known as nanocrystals or nanoclusters). In a single-electron device, the data will be transmitted not by tiny currents, but by single electrons that hop from one quantum dot to the next. It has been found that quantum dots, similar to bulk semiconductors, can radiate light when galvanized with protons or with an electrical current. Therefore semiconductor quantum dots exhibit potential use in future opto-electronic devices.

Other processes

Plating for miniaturized components – micro of nanosytems where improved control over the scale through the combination of computer controlled pulse deposition, ultrasonically enhanced deposition or the use of magnetic fields may open up new areas for low cost wet processing.

Emerging technologies are sono-chemical production of nano magnetic particles, organic molecules assembly to produce molecular controlled semiconductor resistor devices, fabrication of ordered assembly nano- and micro-particles in order to create novel electro-n and opto-materials.

Post Moore's Law - Nanoelectronics and Molecular Electronics.

The rate of increasing performance and components density can be accelerated by molecular electronics. As cited, the growth of semiconductors performances successfully forecasted by an empirical law well known as the "Moore's Law". However, as Moore's law is based on the shrinkage of CMOS transistors, it will be limited by the fundamental laws of physics, starting with backend influences (parasitic resistance and capacitance) and following with effects, which will modify the transistor behavior when the size will decrease to quantum size. Molecular Electronics, will allow either to possibly extend the Moore's Law by providing devices both new and smaller than CMOS or to investigate other forms of information processing. Structured approach is proposed, based on the joint development of expertise from molecular synthesis to computing architecture through templating and assembly to organise molecular devices or the part of the molecule into a single chip. These goals would be achieved by addressing domains as wide as chemistry for synthesis, physics to understand device behavior but also nanomechanics and possibly biochemistry to manipulate molecules and computer architecture to define new information processors. Memory units based on quantum dots were already fabricated in laboratories.

The Approach for nano-electronics

The approach for nano electronics is based on building from bottom up. The optimal way is the building by self-assembly, where the information is present in a limited number of building blocks that allow the spontaneous formation of such well-defined monodisperse species.

The positioning in space requires that the information should be present in the assembly that allows their own confinement at the desired place. That process could be defined as self-organisation.

The self-assembly and self-organisation strategies have to be developed that enable the easy formation of complex patterns.

An important key is probably played by self-assembly of monolayers on (flat) surfaces and at the same time self-assembly of the various species in this layer.

The fabrication of patterns with nanometer dimensions forms a real challenge for material scientists. Most aspects of assembly and self-organisation, such as positioning of functional groups and their recognition properties, are better developed for organic materials than for inorganic ones, whereas the electronic properties of the latter are much better understood. It is, therefore, envisaged that especially the combination of the different material types will lead to fruitful new approaches.

It may be the case that assembly will take place via recognition of organic parts followed by derivatization with inorganic materials, or that small inorganic units modified with organic anchoring points are assembled into circuits in a single process.

At the ultimate limits of fabrication, molecular and atomic approach is advantageous in terms of achievable density and miniaturization.

It is in this crucial area of interfacing and demonstration of devices that the future progress of molecular nanoelectronics lays. Therefore self-assembly technologies have become an increasingly popular way of making nanostructures. Many examples of self-assembly can be found in the world of organic chemistry, and the ancient technique of fabricating Langmuir-Blodgett films has been successfully employed to create structures with specific transport behavior. Moreover, the chemical synthesis of molecules can be viewed as a "self organizing" way to make large numbers of completely identical nanoscale objects. Also in compound inorganic semiconductors, better known to the semiconductor world, self-assembly is a hot research challenge.

It should be realized that for creating useful transport devices, the self-assembled structures must be connected to the outside world in a sensible manner. This issue does deserve a lot more attention than it has enjoyed so far, as it may be a key impediment for use in commercial applications.

Biomaterials - Healthcare Applications.

Biomaterials are the materials that would come into contact with biological environment. For solid biomaterials, the contact is mainly at their surface. Therefore, surfaces of biomaterials need technological solutions in order to facilitate matching of their characteristics with those of their environment.

One of the main approaches in developing advanced Biomaterials is the "design for function", from molecular level into the whole system.

BIOCOMPATIBILITY

A variety of implants are used to replace missing organs or to support mechanical function in the body. If the surface of those implants is incompatible with the body, the implants are rejected. Therefore, it is essential to provide the implants with biocompatibility characteristics.

• Cardiovascular – stents

Stents are made of metals such as stainless steel or nickel-titanium alloys. Bare metal stents are known to promote processes, which lead to re-blockage of the arteries (restenosis). Restenosis is a major problem with the stent procedure. Multilayer coatings have been developed in order to confer to metal stents the required biocompatibility characteristics. In recent years physicians have used such types of stents. Further innovation is to integrate in the coated layer a drug substance that would cure any fault caused to the artery by the stent, which eventually leads to restenosis. The use of bare stents has 30% danger for restenosis. There are statements that the coated stent reduce this rate down to 10%. Currently, coated stent is priced twice the non-coated one, and the drug-integrated coated stent priced triple the non-coated one.

• Orthopaedics – hips, knees etc

An orthopedic procedure is to replace broken or injured limb by implants that can function as the original one. The material used has the mechanical properties similar to those of the original limb, and should function as the original one. The surface of the implant should be biocompatible, and permit the merging of the implant with the surrounding tissues. Some implants are made of Titanium alloys coated with oxides. The optimal coating material and technologies for the various implants are still to be developed.

SURFACE PERFORMANCE

• Molecular level – proteomics etc.

Self-assembled DNA and proteomic microarrays, the thin-film technology could open new markets. The rapid and efficient thermoelectric control provided by ANSER could enable a 100-fold increase in fiber optic switching speed. It could encourage development of electro-holographic router switches and lead the way to all-optical networks. In the life sciences, precise control of thermoelectric devices could make possible faster and lower-cost DNA microarrays. Proteomic chips that would produce messenger RNA and translate it into proteins. (Reed business information, Science and medical group, Oct. 2002)).

DNA, the software for all living things, can also be utilized as a structural proteomic system, and a "logical" component for molecular computing. The example configuration shown here is one of many developed by Ned Seeman at NYU, and others exploring similar concepts. (The NanoBiology Imperative, *www.technofutures.com/nanobio.html*)

SENSORS (INCLUDING BIOSENSORS)

• 'lab on a chip'/ biochips

Biochip is an electronic chip that utilizes biological molecules as the active components.

Pharma companies are motivated to become customers and partners of biochip companies because these companies have technologies that might help the big pharma companies become more productive and deliver more products, in a shortened time development frame. Accelerating the drug making process means turning to modern industrialization of R&D, using genomics and proteomics technologies, and other capabilities that bio-chip companies can provide.

Various types of biochips:

DNA chips are functionalised with thousands of specific genetic sequences. They are used to analyse gene mutations and gene expression in response to a number of stimuli (environment, drugs, stress, cancer, development). On a single chip, all human genes can be analysed in a single experiment.

LabOnChips are miniaturized laboratories automating complex sample preparation and high throughput analysis.



Wafer with 24 labs on chips, source: Laboratoire d'Electronique de Technologie de l'Information

Cell On Chip are microsystems integrating live cells and offering researchers revolutionary ways to monitor and manipulate individually thousands of cells.

• Information processing with biomolecules

Microelectronics utilizes switching devices for electronic data processing. When using currently available technologies, the reduction of switching units to less than 50 nanometers causes electronic and electromagnetic interference, as well as lack of ability to dissipate locally produced heat.

Molecules do not produce heat and do not cause electromagnetic interference and, as such, have been suggested to serve as basic components in molecular electronic devices. Such molecules are now designed using molecular engineering techniques.

Biological molecules have built-in intelligence. Therefore, they can play an important role in data processing and logic operations.

Enzymes are proteins that have built-in some of the basic characteristics required for performing the above-mentioned duties. Their size is around 50-60 angstroms. Enzymes have an active site, on the inner side of their C configured shape.

Enzymes, when appropriately modified, can act as molecular switches and also as components of logic gates, responding to light. Their activity can therefore be controlled by light signals of appropriate wavelengths.

Such molecular devices can act as logic components in bio-electronics circuitry.

Conclusion

Surface technology is a major contributor to the high-tech and to modern industry. The paper describes functional coatings and surfaces for selected industrial sectors, for the short and long-term years. Developments in the application of this technology influence the society and the life quality of people. The production of functional coatings and surfaces enhances technological and economical leverage to the coating and finishing industries. The international R&D effort should target its activities towards this domain and its exploitation in the various industries.

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