THIN FILM DEPOSITION TECHNIQUES – STEPS TOWARDS MORE SUSTAINABLE PACKAGES

Mika Vähä-Nissi[1], Terhi Hirvikorpi[1], Tuomas Mustonen[1], Maarit Karppinen[2], Ali Harlin[1]

[1] VTT Technical Research Centre of Finland, Espoo, Finland
[2] Laboratory of Inorganic Chemistry, Aalto Univ. School of Sci. and Tech., Espoo, Finland

ABSTRACT

A growing trend in packaging industry is towards more sustainable light-weight packaging materials that are not interfering with the end-of-life or energy/material recovery schemes in use for the packaging and production waste. Packaging materials often consist of layers of different polymers and aluminum foil, which makes sorting, and material and energy recovery challenging. Simultaneously, there is an increasing interest in renewable material solutions, which could open up new possibilities for fiber-based materials and various biopolymers. These trends require new approaches in order to improve the functional properties of the packaging materials for more demanding packaging applications.

There are various means, such as nano-sized fillers and encapsulation, to improve the barrier properties and to create functionality. Although montmorillonites, i.e. nano clays, enable thinner layers of specific polymers to give improved properties, this improvement is not sufficient to turn biopolymers into efficient moisture barriers. In this presentation some thin film deposition techniques will be presented as tools for applying thin functional layers at the nano-scale on different surfaces for various applications. Specifically, feasibility of different techniques for packaging applications and/or fiber-based materials will be estimated. This will include recent examples of the development and on-going research work in this area.

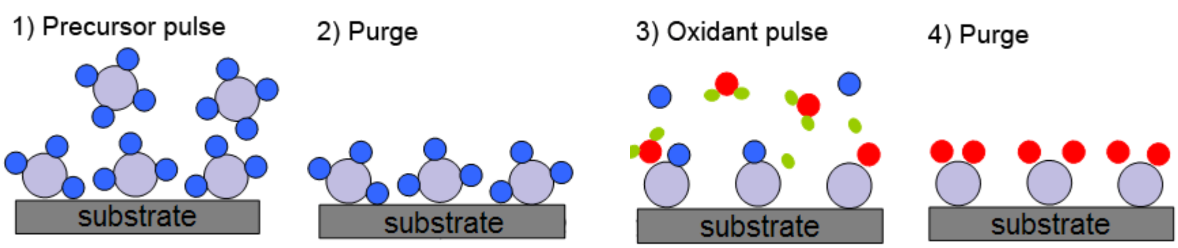

Figure 1. Self-limiting oxide film growth via alternate saturative surface reactions (Picosun Oy).

Atomic Layer Deposition (ALD) is an interesting technique due to recent process and material developments. ALD is used to produce high quality thin layer coatings having excellent barrier properties. It has been applied commercially for processing of e.g. solar cells and planar displays. ALD is a surface controlled layer-by-layer thin film deposition process based on self-terminating gas-solid reactions (Fig. 1) usually applied to create thin nanolayers of inorganic compounds. Recent development of the technology, like continuous operation mode, has made it possible to extend the use of ALD for new applications like high barrier polymer films. There are already patent applications concerning a roll-to-roll process [1-4]. VTT has also previously reported successful ALD deposition onto synthetic and bioplastic films and coatings achieving marked improved barrier properties against water vapor and oxygen [5-7].

Diamond-like carbon (DLC) and different hybrids can be deposited with various techniques [8,9]. DLC is a group of hard and chemically inert materials consisting of carbon bonded partially as diamond and partially as graphite. Gas barrier of DLC films have been investigated for food packaging such as an inner coating for e.g. plastic bottles. One obstacle for the application of DLC coatings has been the lack of adhesion to the substrate as the coating thickness is increased. The advantages of DLC over silicon oxides are related to flexibility and recyclability [10]. The high packing density of DLC provides a physical resistance to diffusion of liquids or gases.

Although CVD normally utilizes high temperatures not suitable for heat-sensitive materials, modified CVD can be also used to produce thin polymeric films on different substrates. Initiated chemical vapor deposition (iCVD) can be used to produce linear polymers. iCVD has been used to polymerize vinyl monomers. Gases are fed into a vacuum chamber where heated wires are used to decompose the initiator into free radicals [11]. The polymerization on the surface of a cooled substrate will then proceed as free radical polymerization. Oxidative CVD on the other hand relies on step growth polymerization employing an oxidant and is used for the deposition of thin films of conducting polymers [12].

Liquid flame spraying, an aerosol method, has been suggested as a tool for creating and applying nanoparticles and nanocoatings on various flexible substrates, such as paper, paperboard and polymer films [13,14]. The idea is to feed small droplets of liquid precursors through a spray nozzle into a flame. While the flame temperature is high, the thermal load on the surface is 100-300 °C. Different gases can be used to create the flame. The droplets evaporate and the precursors may react to form nanoparticles. The gas and particle flow is then subjected to the surface to be coated. Functional properties provided could be conductivity or barrier properties. Increased line speed decreases the thermal effect on the substrate. For example, nano TiO_2 is used for hydrophobicity and SiO_2 for hydrophilicity.

While plasma depositions are usually made at low pressure, recent research is directed towards coating at atmospheric pressure, simply because it can be implemented as part of an in-line processes. In atmospheric plasma, ionized gas and radicals are separately produced from a mixture of the carrier gas and chemical precursor and blown onto a substrate. A typical application is the deposition of siloxanes for their barrier, hydrophobic and release properties. The main challenges are related to the complex reactions in the plasma and the deposition speed and uniformity.

In addition to the methods listed above, there is a whole set of engineered biohybrid coatings. In these coatings enhanced properties are achieved by combining chemoenzymatic modification methods with organized coating structures or formation of controlled assembly through high shear deposition. This allows interesting combinations of biopolymers and nanoparticles for e.g. barrier purposes.

There are thus several alternatives for creating nano coatings or coatings utilizing nano-scale features. Techniques, such as ALD, provide possibilities to enhance the properties of various sensitive materials including papers, polymer films and coated papers and boards. Motivation for such solutions include enhanced sustainability through light-weight packaging materials and lower impact on material and energy recovery compared e.g. to aluminum foil.

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Thin film deposition techniques
– steps towards more sustainable packages

Dr. Mika Vähä-Nissi[1], Terhi Hirvikorpi[1], Tuomas Mustonen[1], Prof. Maarit Karppinen[2], Prof. Ali Harlin[1]

[1]VTT Technical Research Centre of Finland

[2]Aalto University School of Science and Technology

Outline of presentation

- Introduction
  - Package and packaging material trends
  - Existing applications for thin film deposition techniques
- Motivation - thin film deposition techniques for packaging
- Examples of thin film deposition for packaging materials
  - Physical vapor deposition (PVD)
  - Atmospheric plasma deposition
  - Liquid flame spray (LFS)
  - Chemical vapor deposition (CVD)
  - Atomic layer deposition (ALD)
- Conclusion

Functions of Packaging

- Contains a specific amount of product
- Enables economically/technically feasible logistics
- Protects contents from various hazards
- Informs supply chain and consumer about packed goods
- Advises the consumer to consume the packed goods

- Sells the package and packed goods to consumer
- Provides the consumer with experience
- Provides easy post-consumption alternatives
- Ensures human and environmental safety

SUSTAINABLE PACKAGING COALITION®

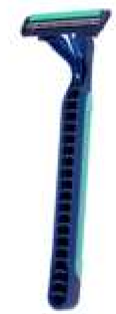
What is sustainability?

- Beneficial, safe and healthy for individuals & communities throughout its life cycle
- Meets market criteria for performance and cost
- Sourced, manufactured, transported & recycled using renewable energy
- Maximizes use of renewable or recycled source materials
- Manufactured using clean production technologies & best practices
- Made from materials healthy in all probable end-of-life scenarios
- Designed to optimize materials and energy
- Recovered effectively and used in biological and/or industrial cradle-to-cradle cycles

Sustainability no longer a buzz word

- Aim to **decrease costs** still there - covering whole supply chain,
  - Thin and light-weight materials sets requirements for improved properties and provides possibilities for emerging technologies,
- From cost reduction towards **renewal** of package/packaging
  - Brand owners look for solutions to reply to need for biobased solutions – also partial replacement acceptable,
  - Emphasis on renewable raw materials, enabling new approaches in addition to conventional biopolymers. New materials must fit to re-use, or recovery schemes,
  - Safety together with small carbon/water footprints essential,
  - Role of interest groups increasing – change of driving forces.

Examples of current thin film applications



Driving forces arise from need

- Packaging materials are typically made of polymer and foil laminates, or different material combinations.
- This makes sorting, and material and energy recovery challenging. Even small amounts of alu-foil ruins recyclability of paper. Production of foil is energy intensive, and under acid conditions aluminum can dissolve causing problems for ecosystem.
- However, packaging trends require improved functional properties of packaging materials for more demanding applications.
- Poor barrier properties, especially sensitivity towards moisture, are main challenges for extended use of fibre-based materials or biobased polymers.

Nanoparticles still face challenges

- Formulation and additives related challenges:
  - Care needed when tailoring particle surfaces for specific polymers
  - Dispersing nanoparticles into (polymer) matrix can be challenging
- Although positive effect is obvious no miracles can be done:
  - While nanoclays interesting in case of PA and PET, effect with polyolefins and several biopolymers more limited
- Developing new modifier for particle surface constitutes new product with related registration costs
- Theories on effect of structure vs. performance partly controversial
- Serious safety, processing and recycling concerns

Physical Vapor Deposited Oxides – state of art

Own experience

- Started / best known as SiO_X less than 50 nm in thickness although also aluminum or mixtures are being used.
- Deposition technologies include physical vapor deposition such as vacuum deposition and sputtering (and CVD and plasma enhanced methods).
    - PET coated by plasma or evaporation. Polyolefins are challenging due to surface roughness and heat sensitivity, and nylon because of water sensitivity
- Applications include lid stock, modified athmosphere packaging, dried soup and other pouches, pharmaceuticals and chocolates, citrus and fruit juices, etc.

Diamond-Like Carbon (DLC) coatings

Own experience, partners

- Barrier coating applied using e.g. RF plasma enhanced chemical vapor deposition CVD typically for plastic bottles
- Acetylene atomized to form 20-40 nm layer quenched on cold surfaces
- DLC resistant to wear as coated layer has structure resembling diamond, but shows some flexibility due to hydrogen in structure
- Find uses in high-speed actions involved in processing foods such as chips and in guiding material flows in food packaging
- Thermal stresses can cause discoloration of polymers
- DLC PET bottles approved by FDA

Plasma NICE

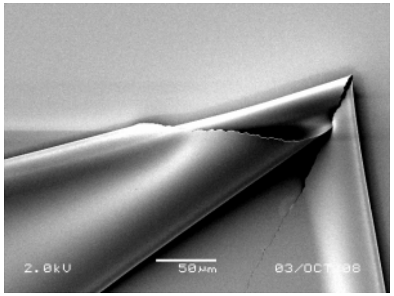
Atmospheric Plasma Deposition

Own activities

- Ionized gas and radicals are separately produced from mixture of carrier gas and chemical precursor blown on substrate
  - Advantages: coatings from nm to μm scale, barrier coatings
  - Challenges: complexity of reactions, speed and uniformity
- Commercially available systems for low speed applications
- Low deposition speed (~150 nm/min)
  - Thin coatings not suitable for coarse substrate surfaces
- Options for high volume, high speed inline applications
  - Development and upgrading of experimental systems
  - Combination of plasma deposition with other treatment/coating technologies: high power pre-treatment and pre-coating

Hot-Wire Chemical Vapor Deposition (HW-CVD)

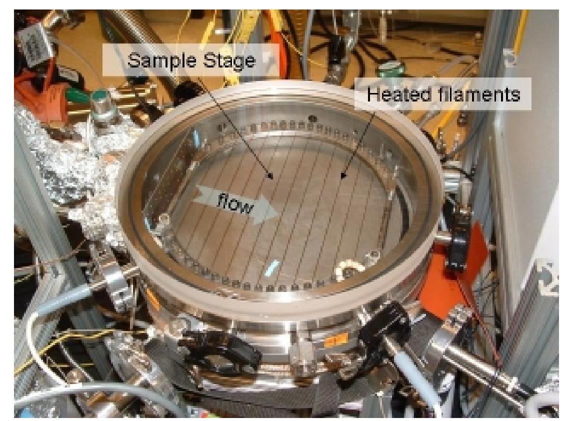
- Deposition of both organic and inorganic thin films
- Hot-Wire or Hot-Filament CVD initially developed for deposition of diamond and becoming mature technique in silicon film deposition
- Resistively heated wires positioned in an array above substrate
- Deposition takes place after catalytic or thermal decomposition of reactant gases at the surface of these heated filaments/wires
- HW-CVD overcomes limitations of CVD:
  - Absence of ion bombardment during deposition,
  - High deposition rates,
  - Lower costs,
  - Easy scalability to large areas.



Initiated Chemical Vapor Deposition

Partners

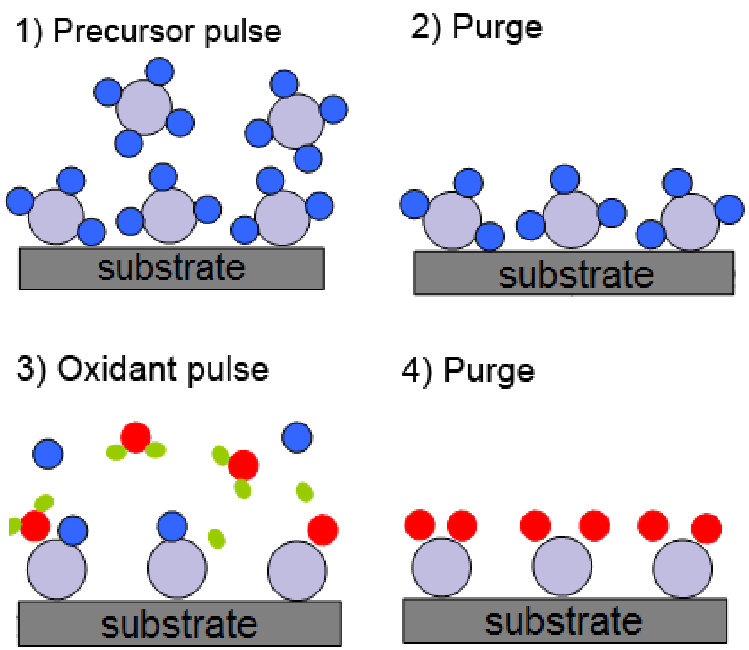
- Initiated chemical vapor deposition (iCVD) is subset of HW-CVD developed for polymeric thin films
- iCVD uses an initiator decomposing into radicals and reacting with monomers leading to in situ surface polymer synthesis and pinhole-free organic thin films having precisely defined structures
- Using initiator leads to high deposition rate and control over film structure composition
- iCVD allows films of nanoscale thicknesses and coating of nanoscale features, as there are no surface tension and non-uniform wetting effects.



Atomic Layer Deposition for precise layers

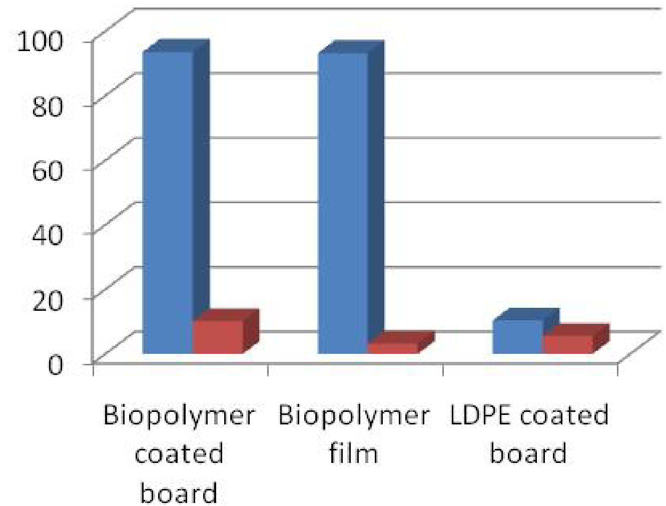
Own activities

Repeated cycles of:



Picosun Oy

Even without optimisation:



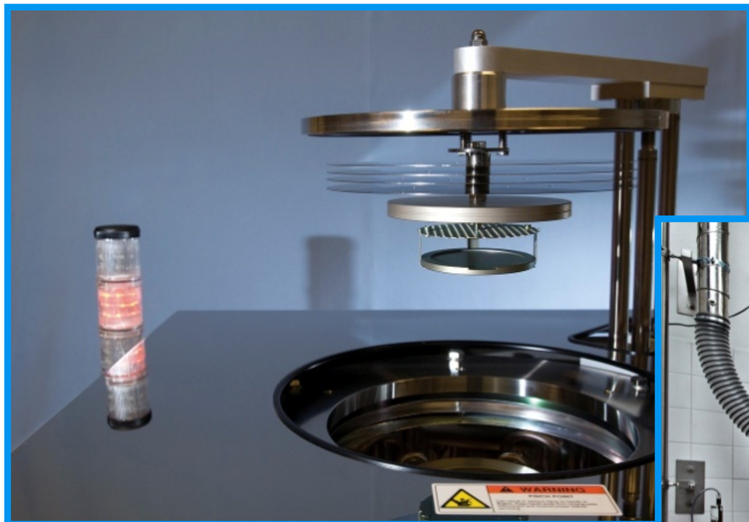
WVTR, g/m^2/d, 23 °C, RH 75%
normalized to 20 µm

Invented in Finland 1974

Examples of recent published/ submitted ALD studies at VTT

- Atomic layer deposited aluminum oxide barrier coatings for packaging materials.
- Comparison of some coating techniques to fabricate barrier layers on packaging materials.
- Effect of corona pre-treatment on the performance of gas barrier layers applied by atomic layer deposition onto polymer coated paperboard.
- Barrier properties of multilayered polyelectrolyte complexes coated with atomic layer deposited Al_2O_3 layer.
- Effect of heat-treatment on the performance of gas barrier layers applied by atomic layer deposition onto polymer-coated paperboard.
- Fibrous product having a barrier layer and method of producing the same, patent application FI 20085937/ WO2010037906

As for now, ALD is batch process..

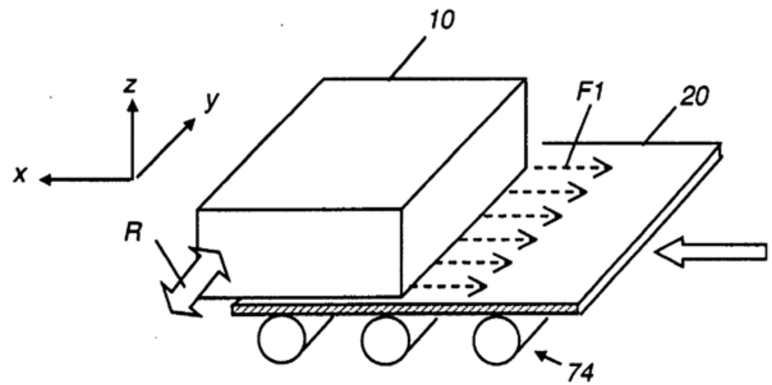


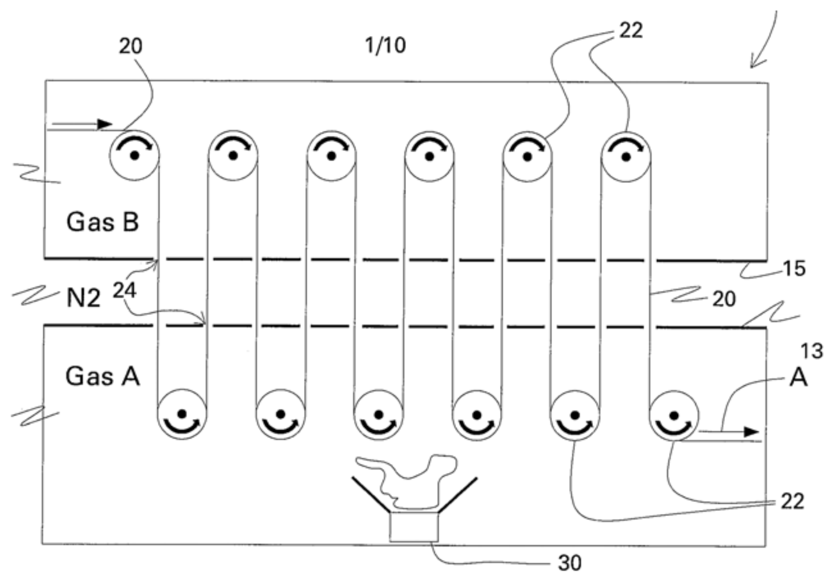
VTT's Picosun SUNALE™ reactor in semi-clean room feasible for e.g. material (paper, board, films) studies

..but there is trend towards roll-to-roll operation

Related patent applications:

- GE Company WO2008057625
- Eastman Kodak US20070238311
- Applied Materials US20040067641
- Planar Systems, WO2007112370
- Several research centres and universities have activities or process solutions - most not related to food packaging.
- Main effort to reduce cycle time and to control gas flows in reactor/die.

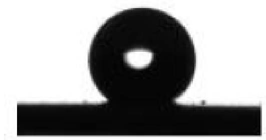




New initiative: Roll-to-roll atomic layer deposition process development (RRALD)

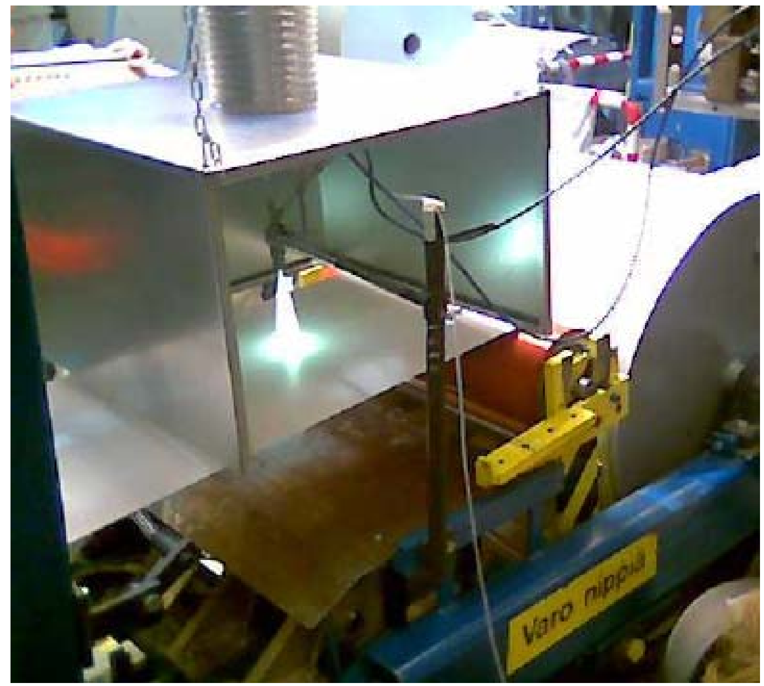
- Three year project started August 2010.
- Goals to develop continuous roll-to-roll process and to develop/ characterize new functional coating structures for packaging.
- Research partners:
  - VTT Technical Research Centre of Finland
  - Advanced Surface Technology Research Laboratory at Lappeenranta University of Technology (ASTRaL)
  - Paper Converting and Packaging Technology, Tampere University of Technology
- Funded by TEKES (the Finnish Funding Agency for Technology and Innovation), Industry and Research partners

CA = 148°



Liquid Flame Spray (LFS) Nanocoating

- Aerosol method for creating & applying nanoparticles and -coatings on substrates (originally glass)
- Droplets of precursors fed through spray nozzle into flame
- Flame is hot, but thermal load on surface is only 100-300 °C
- Droplets evaporate and precursors react to form nanoparticles
- For example, TiO_2 for *hydrophobicity* & SiO_2 for *hydrophilicity*.



Conclusions

- Trend in packaging both overall cost reduction along supply chain and renewal – sustainability becoming increasingly important.
- Replacing environmentally less favorable packaging components, using biomaterials and thin/light materials require enhanced functional properties.
- Simultaneously, basic functions of packaging are widening.
- Nano particles used to upgrade plastics face certain challenges.
- There are wide variety of thin film deposition techniques with typical current applications outside of packaging field.
- On-going research activities indicate thin film deposition techniques, such as ALD, provide interesting possibilities for fibre-based substrates and packaging materials.