Photocatalytically active surfaces produced by atmospheric processes

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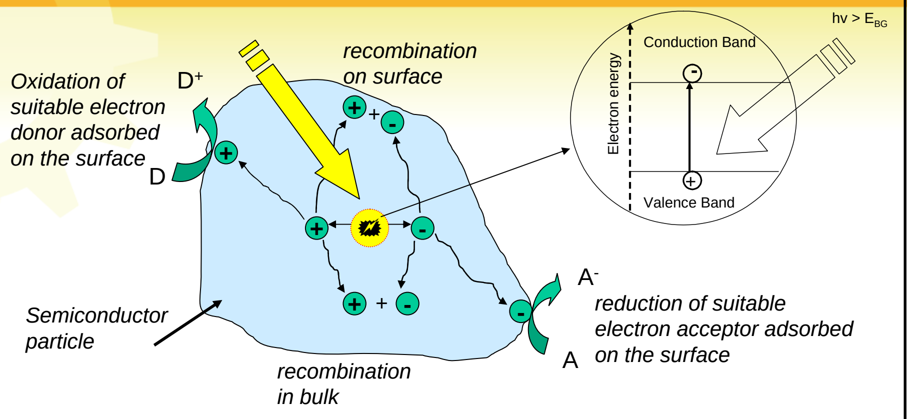
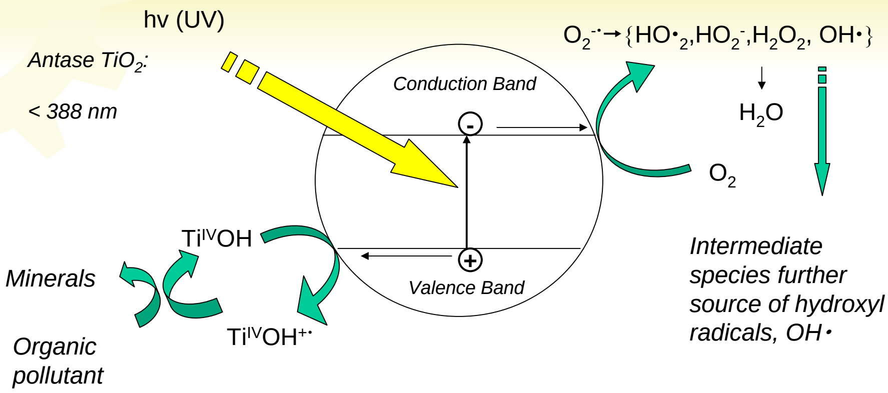
Outline

1. *Semiconductor photocatalysis*
2. *Titania as photocatalyst*
3. *Atmospheric deposition techniques*
4. *Liquid flame spraying*
   - *titania*
   - *titania composite deposits*
5. *Suspension spraying*

Major processes caused by the absorption of ultra-bandgap light in semiconductor particle

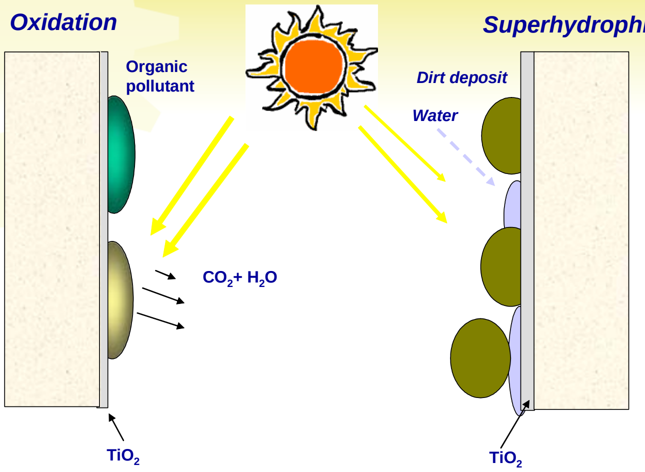


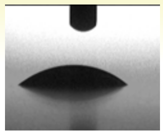
Major processes in photomineralization of organics by TiO_2 semiconductor



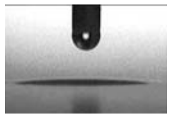
also important photo-sterilization and photoinduced superhydrophilicity

Two different cleaning mechanisms of photocatalytically active TiO_2 surfaces





Water droplet on TiO_2 surface before UV exposure



Water droplet on TiO_2 surface after UV exposure

(Pictures fron Laboratory of Inorganic Chemistry, Helsinki University, V. Pore)

Deposition of TiO_2 coatings on different surfaces

TiO_2 coatings can be deposited by almost all known deposition techniques;
- different modifications of CVD and PVD (plasma, laser or microvawe assisted)
- chemical technique; sol-gel widely used

If we are aiming to use these coatings industrially on large surface areas atmospheric pressure open air techniques are interesting;

- Liquid flame spraying
- Suspension spraying of nanoparticles
- Thermal spraying

Definitions

Chemical vapour deposition (CVD):

- *constituents of the vapour phase react chemically near or on a substrate surface to form a solid deposit*
- *occurs at elevated temperatures (furnace, remote heating; rf-induction, high-intensity radiation lamps*
- *plasma, microwave, photo, laser, rf, and electron-enhanced CVD-processes exist.*

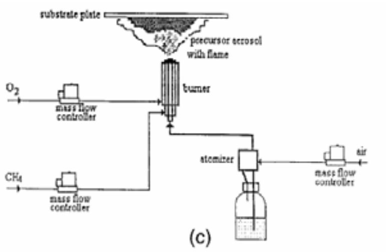
Combustion CVD: *(A.T. Hunt et al. Appl.Phys. Lett. 63(1993)266)*

- *vapour deposition of a film near or in a flame which causes the precursors to react chemically*
- *precursors are dissolved in flammable solvents, which are sprayed through burner.*
- *for oxides oxygen is supplied by the oxidant gas or the surrounding gases or the dissolved chemical reagents (e.g. titanium isopropoxide)*

Definitions

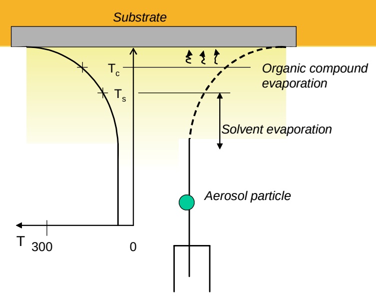
Liquid flame spraying (LFS) or Aerosol assisted chemical vapour deposition (AACVD):

- *liquid precursors are sprayed inside a flame (eg. oxygen/hydrogen) in which they react to form nanoparticles or evaporate to produce gaseous precursors for film deposition*
- *heat is produced by the flame*



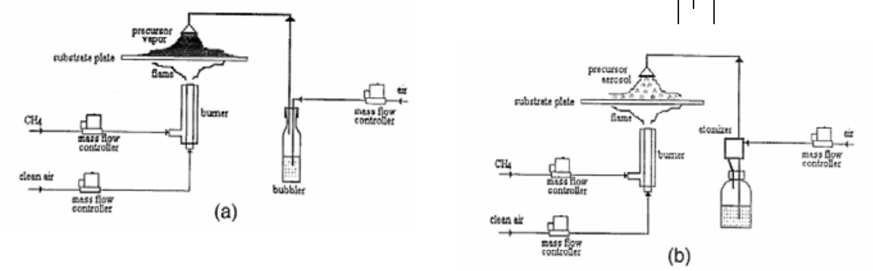
G.Yang, P.Biswas, P.Boolchand and A.Sabata, J.Am.Ceram.Soc,82(1999)2573

Definitions



Spray pyrolysis:

- liquid precursors are evaporated near the heated surface and react on the surface to form a deposit



G.Yang, P.Biswas, P.Boolchand and A.Sabata, J.Am.Ceram.Soc,82(1999)2573

Deposition mechanisms in AACVD

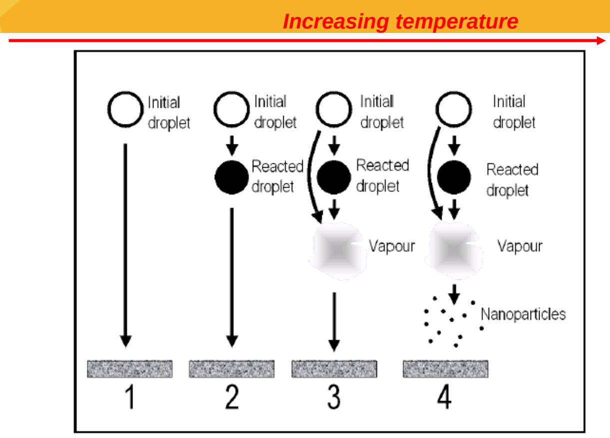
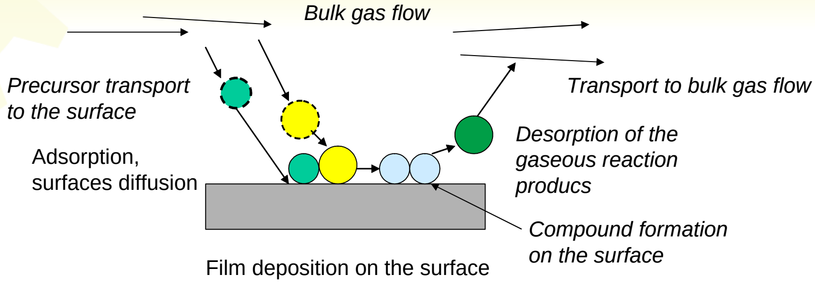


Figure 1. A schematic of different possible routes of material deposition in Aerosol Assisted CVD (according to Choy, 2003). Process 1 denotes for low temperature and process 4 for a high temperature.

H. Keskinen, et al., J. Nanoparticle Research, in print

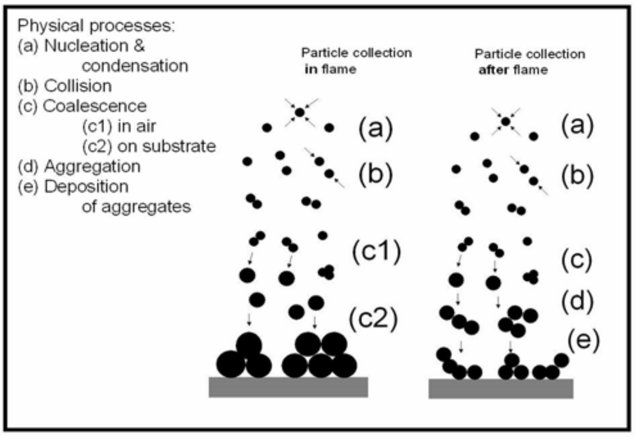
Deposition mechanisms

Conventional CVD



Deposition mechanisms

Nanoparticle formation in the gas phase and deposition on the surface



M. Mäkelä, et.al. Mater. Lett. 60 (2006) 530-534

Open air plasma CVD of TiO_2

Another option

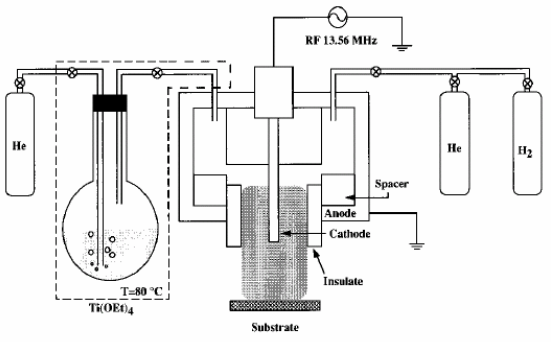


FIG. 1. Schematic diagram of cold plasma torch used for TiO_2 film deposition.

Dep. rate at 200 °C~ 200 nm/min
at 450 °C~ 900 nm/min

Anatase/rutile T > 350 °C

H.-K. Ha et al., Appl.Phys.Lett. 68(1996)2965

Liquid Spray Mist CVD of TiO_2

B.-H. Kim et al. Materials Science and Engineering B107 (2004) 289-294

TiO_2:
- *amorphous at < 300 °C*
- *anatase above 400 °C*
- *deposition rate ~ 10 nm/min*

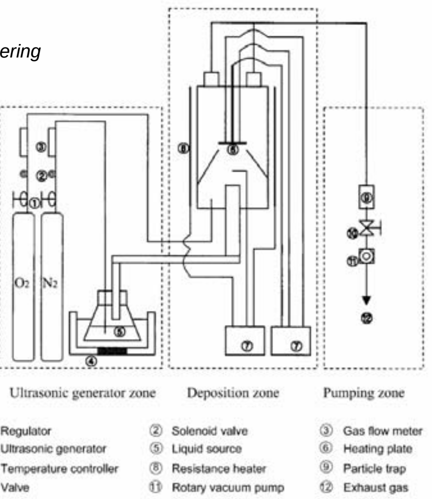


Fig. 1. Schematic diagram of the apparatus for TiO_2 thin film deposition using the liquid mists generated by ultrasonic atomizer.

Titania nanoparticle and thin film synthesis by liquid flame spraying

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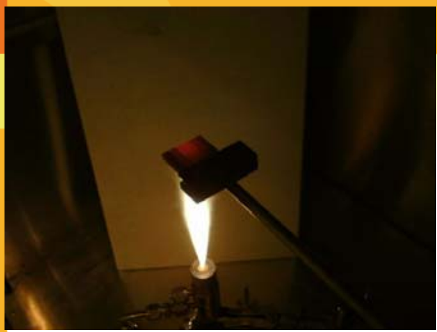

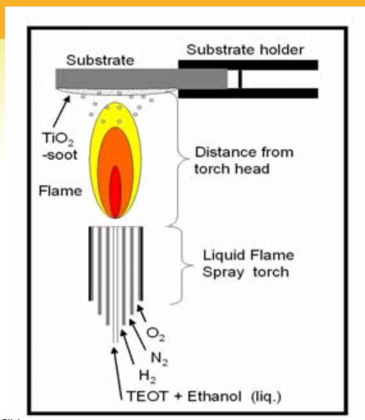

Liquid precursors: TEOT, TTIP
Oxygen/Hydrogen flame

Aerosol Physics Laboratory, Tampere University of Technology

J. Mäkelä, S. Hellsten, J. Silvonen, M. Vippola, E. Levänen and T. Mäntylä, Collection of liquid flame spray generated TiO_2 nanoparticles on stainless steel surface, Mater. Lett. 60 (2006) 530-534

Deposition options in liquid flame spraying

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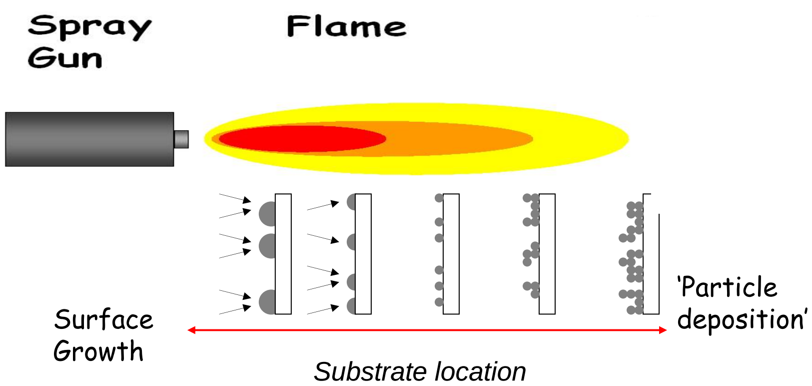
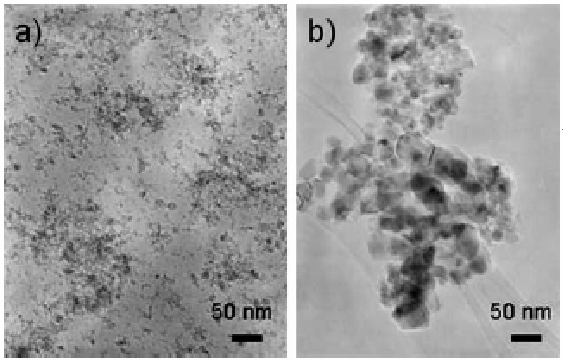


Particle size and morphology

On TEM grit 1 s.

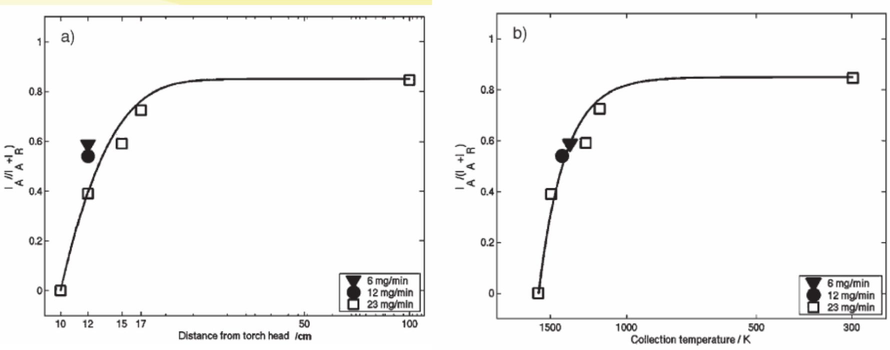


On stainless steel, 30 min

Fig. 5. TEM-micrographs of (a) fast sample: particle collector with TEM grid was swept through the flame (15 cm, 23 mg/min) within 1 s and (b) material on stainless steel substrate (15 cm, 23 mg/min), residence time within flame is 30 min. $T = 1200$ K.

M. Mäkelä, S. Hellsten, J. Silvonen, M. Vippola, E. Levänen and T. Mäntylä, Collection of liquid flame spray generated TiO2 nanoparticles on stainless steel surface, Mater. Lett. 60 (2006) 530-534

Effect of collection distance and temperature on anatase/rutile ratio



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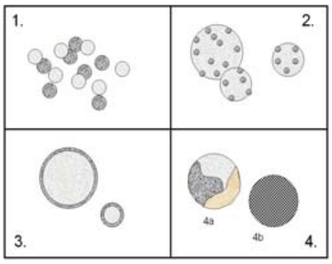
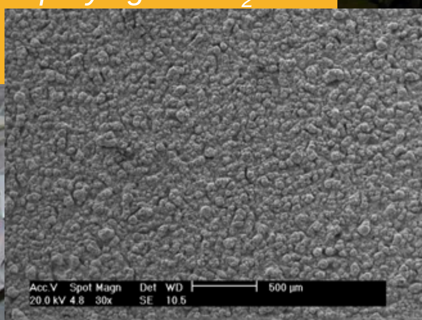
Deposition of TiO_2 composite nanoparticles by liquid flame spraying

Process can be used also for composite TiO_2 deposits and coatings



- *Me-TiO_2 or oxide/TiO_2*
- *to the yield of surface activity and the rate of the photocatalytic reaction*

Suspension spraying of TiO_2

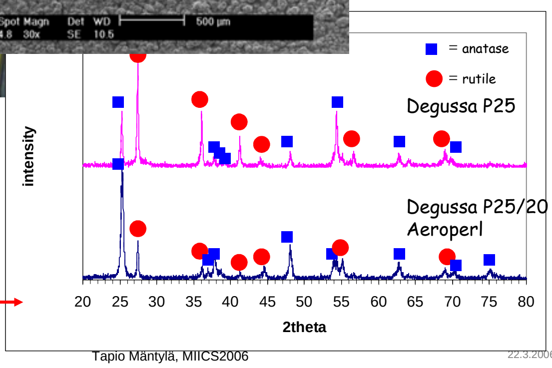


(S. Veräjänkorva)

HVOF spraying

Nanoparticle suspension in ethanol

Mixed anatase/rutile structure



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Domain Materials

» PHOTOCATALYTIC TECHNOLOGIES AND NOVEL NANOSURFACES MATERIALS – CRITICAL ISSUES «

PHONASUM

2006-2009

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Institute of Materials Science, Tampere University of Technology

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