Manchester Metropolitan University

Functional Films by Magnetron Sputtering Processes

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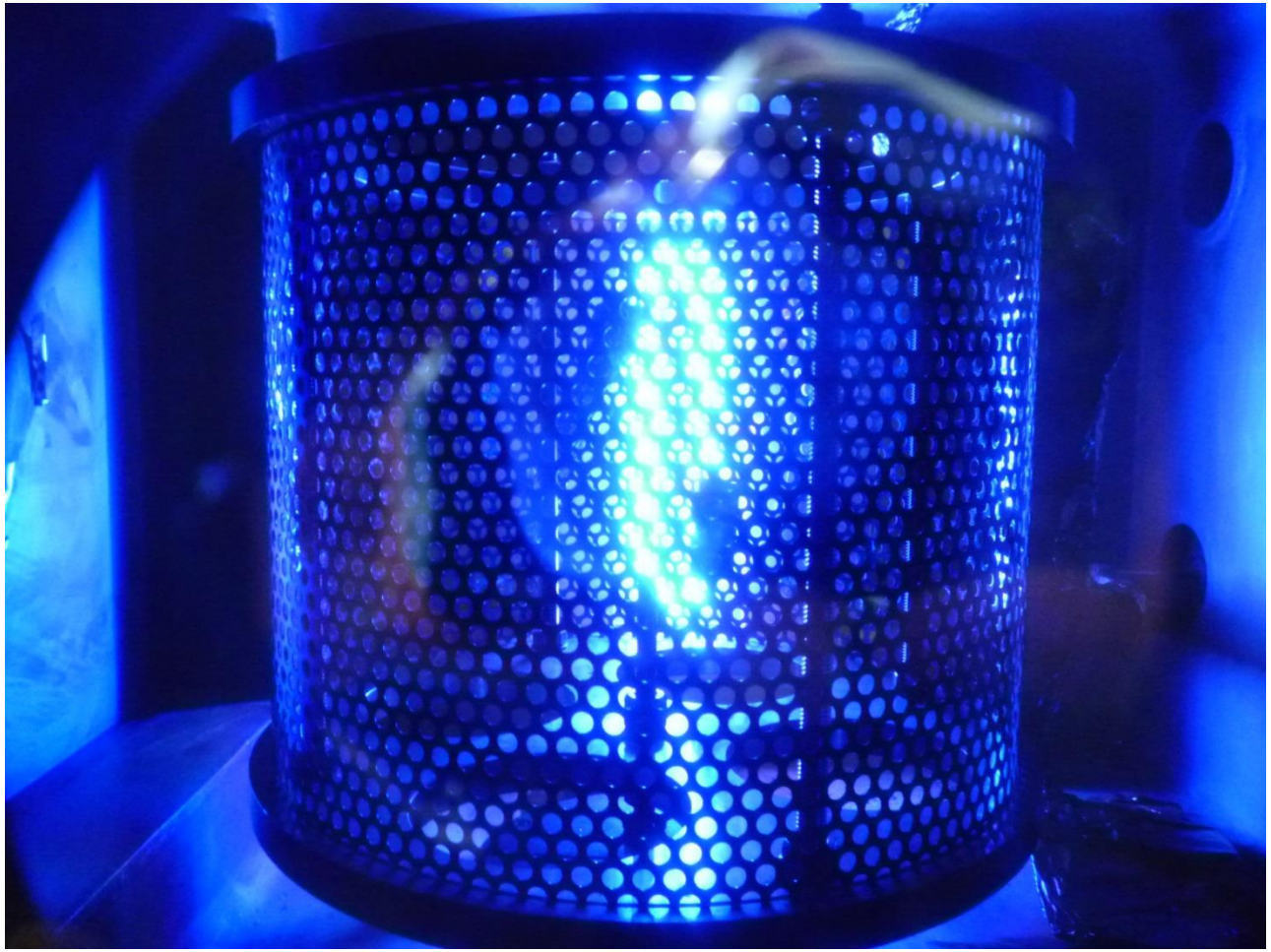
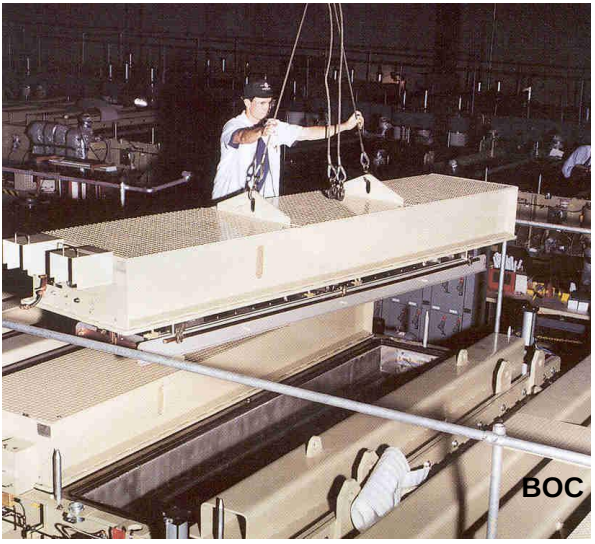
Magnetron Sputtering

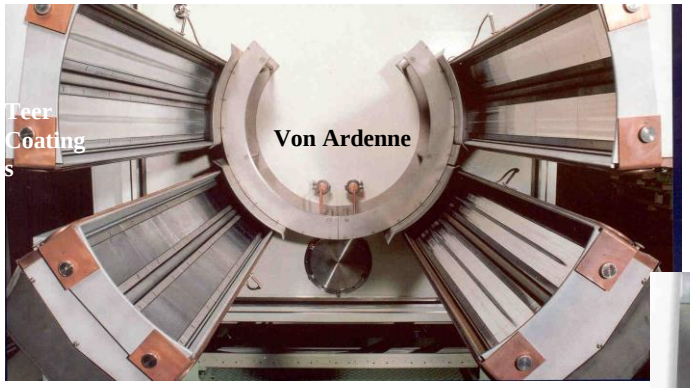
- **Versatile PVD technique for high quality coatings**
  - **Metals, alloys, oxides, nitrides, multi-layers, etc.**
  - **Magnetron discharge driven in DC, pulsed DC, HiPIMS, RF, MW, AC modes**



Magnetrons:

- Rectangular, circular, or cylindrical
- 10s of mm diameter up to several m in length
- Variable field strength – variable ICD to growing film
- Multi-source systems – vertically opposed, in-line, web coating, indexed, etc.

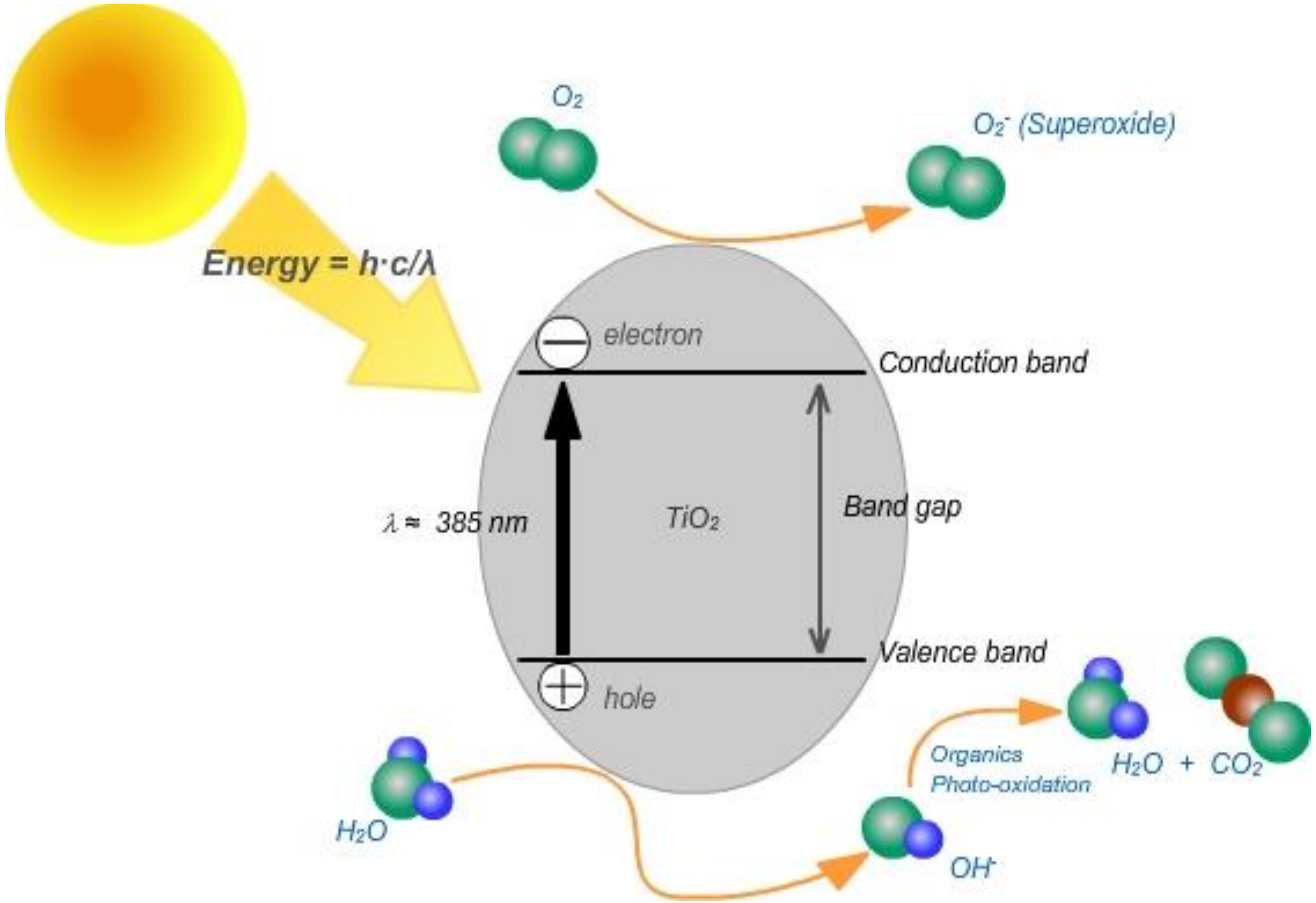




Industrial Applications of Magnetron Sputtering

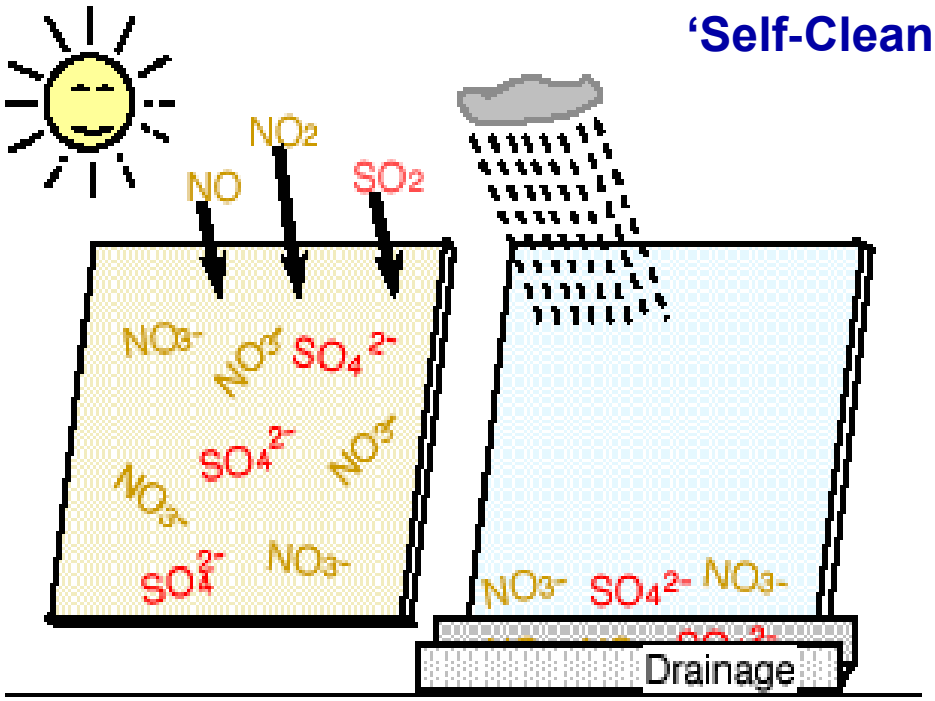
- Wear resistant coatings on cutting tools/components
- Low friction coatings
- Corrosion resistant coatings
- Decorative coatings
- Architectural & automotive glazing
- Anti-reflective/Anti-static (AR/AS)
- Transparent conductive oxides (TCO's)
- Microelectronics
- Data storage media

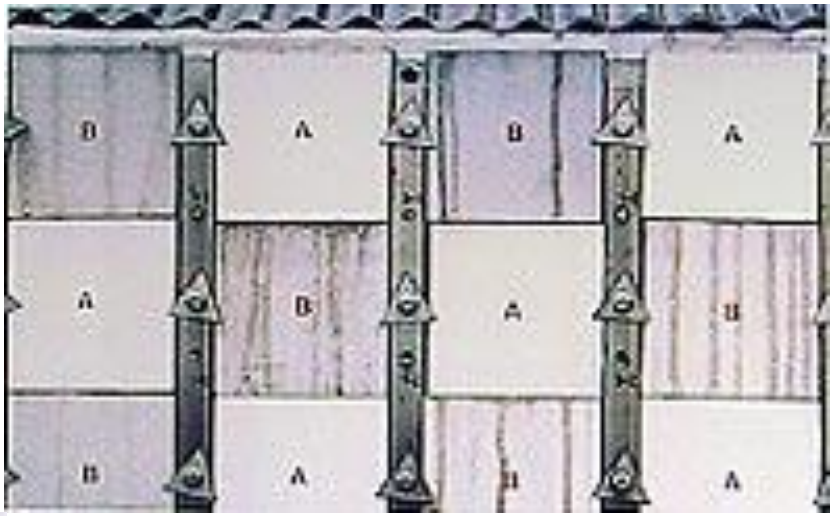
Case Study 1: Photocatalytic and Superhydrophilic Titania Coatings



Photocatalytic and Superhydrophilic Applications

‘Self-Cleaning’ Surfaces





Anti-fogging surfaces

Photocatalytic and Superhydrophilic applications of TiO_2

- Eye glasses;
- Mirrors;
- Car side-view mirrors

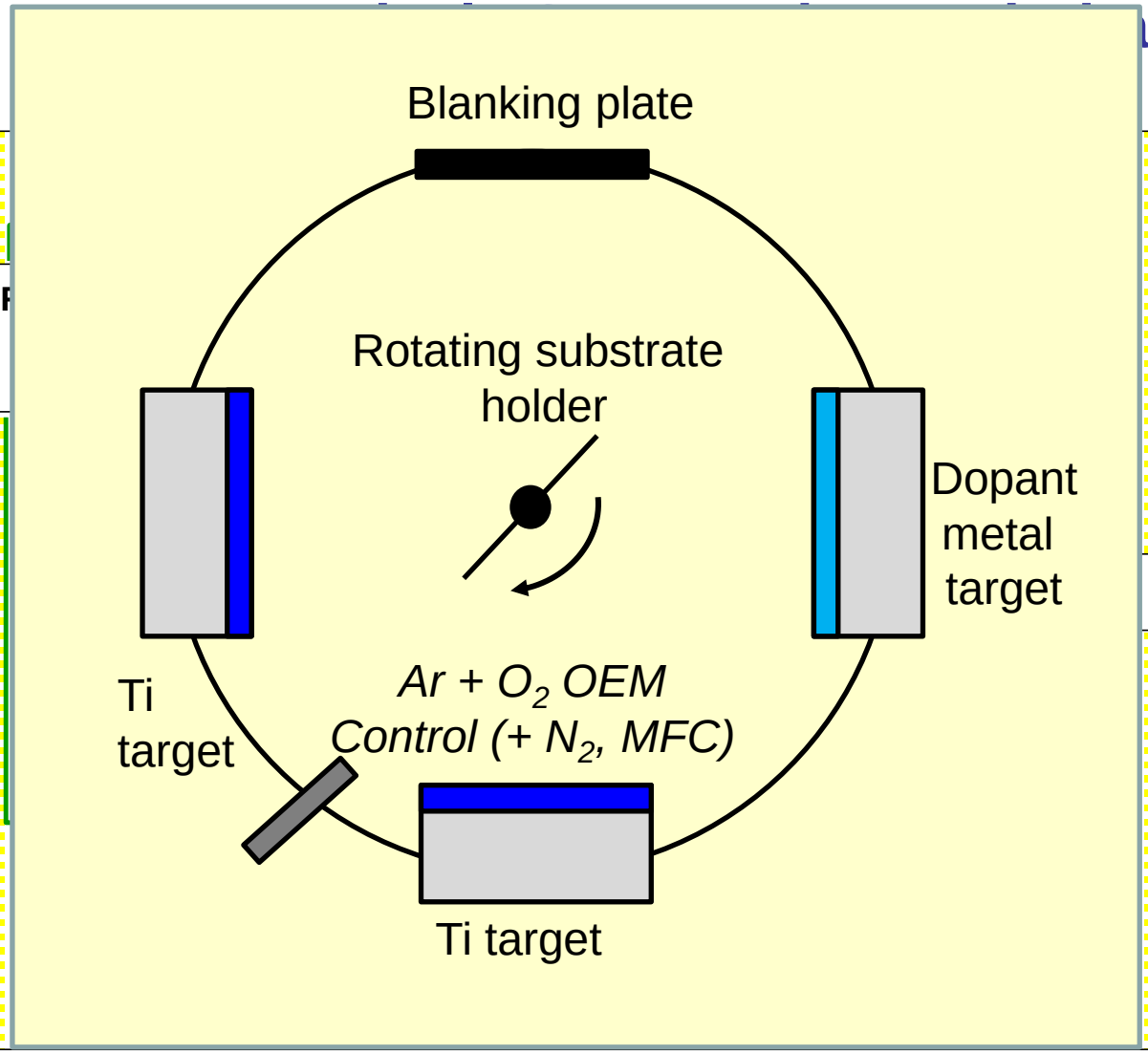
- Implants;
- Medical instruments;
- Indoor tiles

- Road pavements;
- Exterior tiles;
- Exterior paint

Highest activity shown by anatase:

- **Requires elevated temperatures for formation;**
- **Requires UV light for activation;**
- **Dopants investigated to promote visible light activity**

...nia Coatings

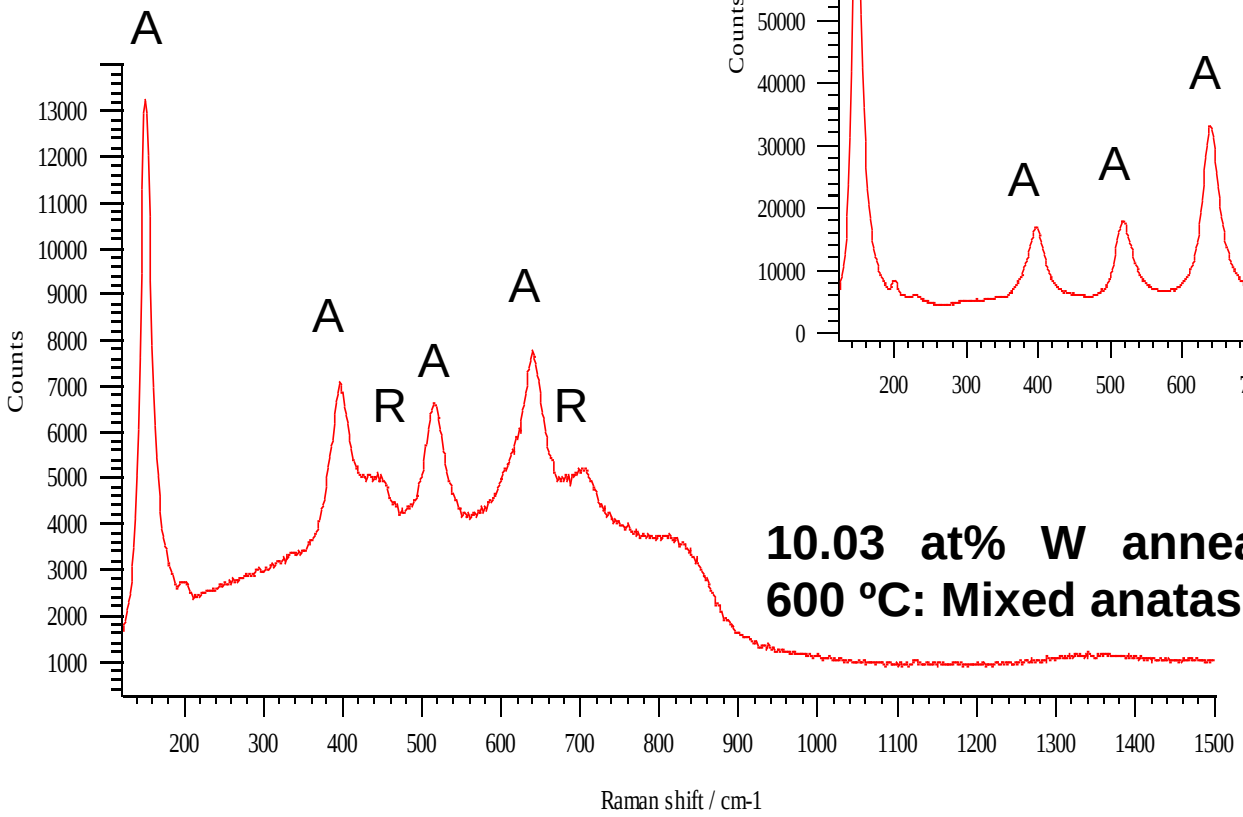


- **Constant power to 2x Ti targets: 1kW pulsed DC**
- **Power to dopant target varied in range 60 to 180W DC**
- **Substrates – floating**
- **OEM control for O_2**
- **MFC control for N_2**

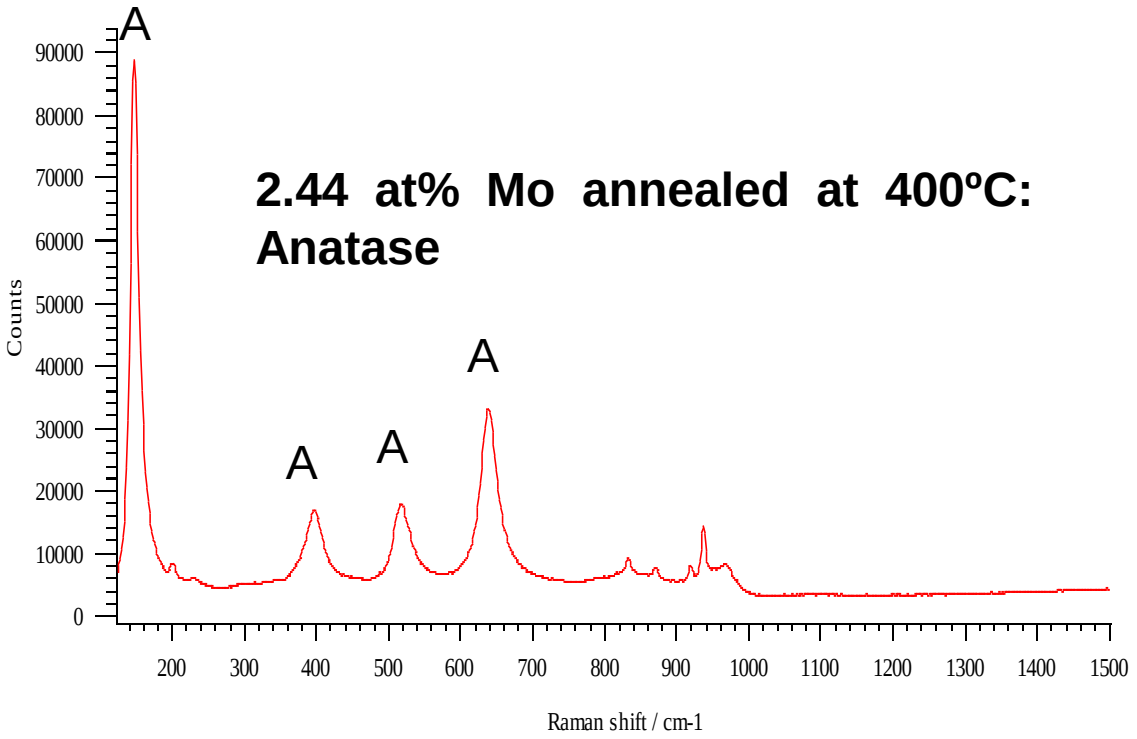
As-deposited coatings analysed by SEM, EDX, micro-Raman spectroscopy. Selected coatings annealed in air at 400 or 600 ^{O}C and re-analysed

Raman Spectroscopy Analysis of PDC Doped Titania Coatings

As-deposited PDC coatings are amorphous



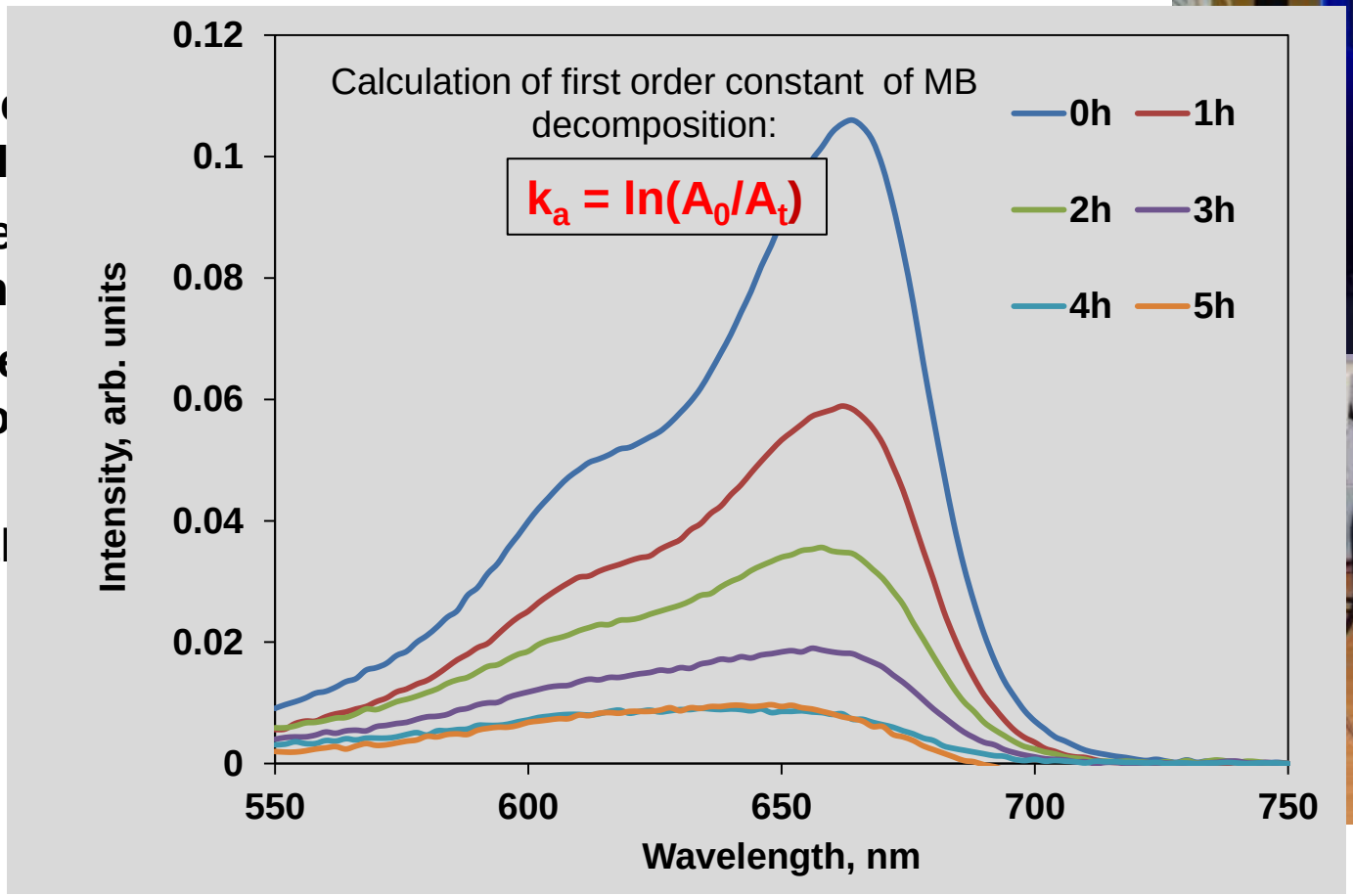
2.44 at% Mo annealed at 400ºC: Anatase

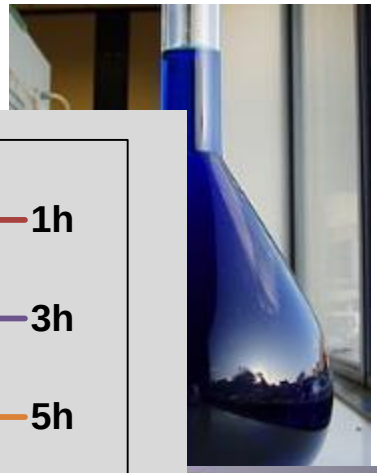


10.03 at% W annealed at 600 ºC: Mixed anatase/rutile

Photocatalytic Activity Tests: Decomposition of Methylene Blue

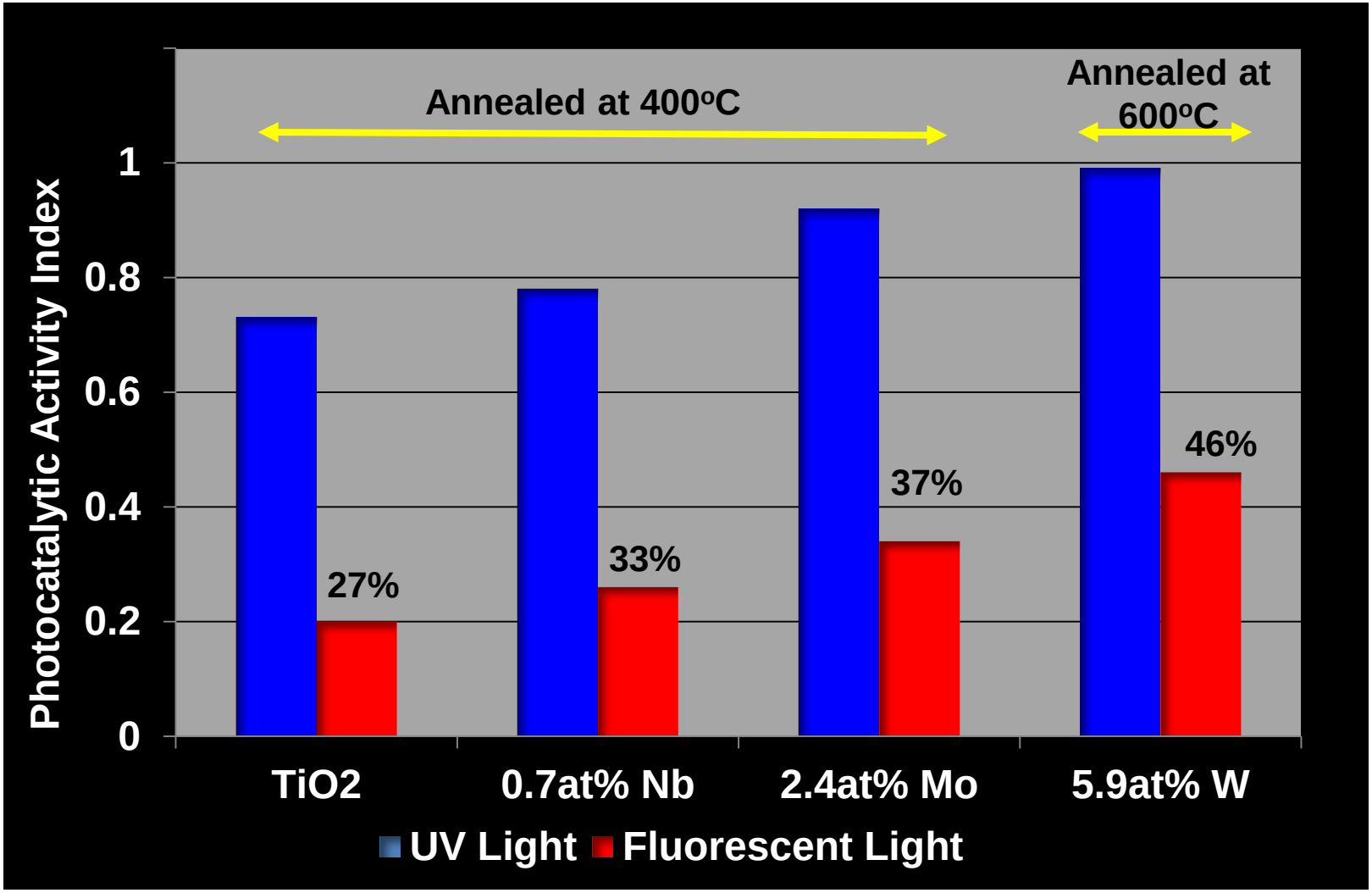
- Methylen
  dye: $C_{16}H$
- Often use
  compoun
- UV-visible
  absorptio
- Changes
  monitor t
  of MB by
  coatings





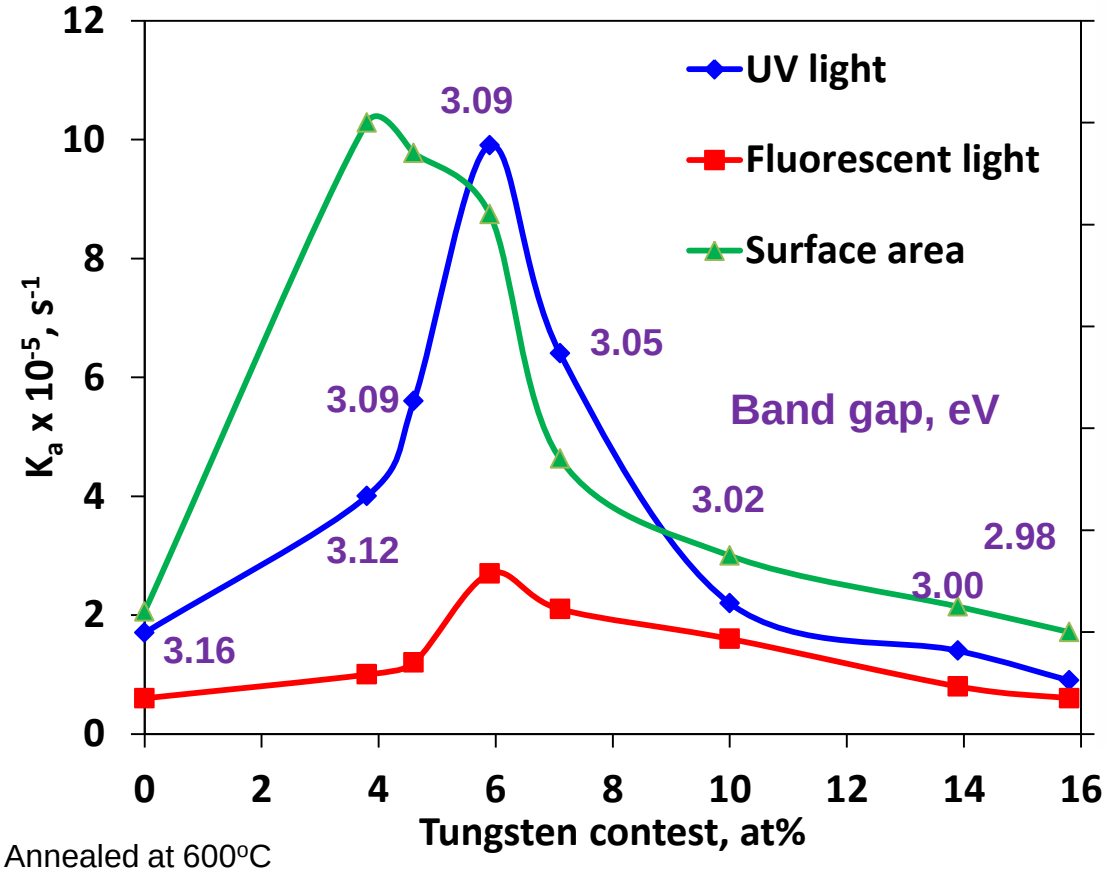
$$C_{16}H_{18}ClN_3S + 25.5O_2 \xrightarrow{TiO_2 + h\upsilon \geq 3.2eV} HCl + H_2SO_4 + 3HNO + 16CO_2 + 6H_2O$$

Comparison of relative activity

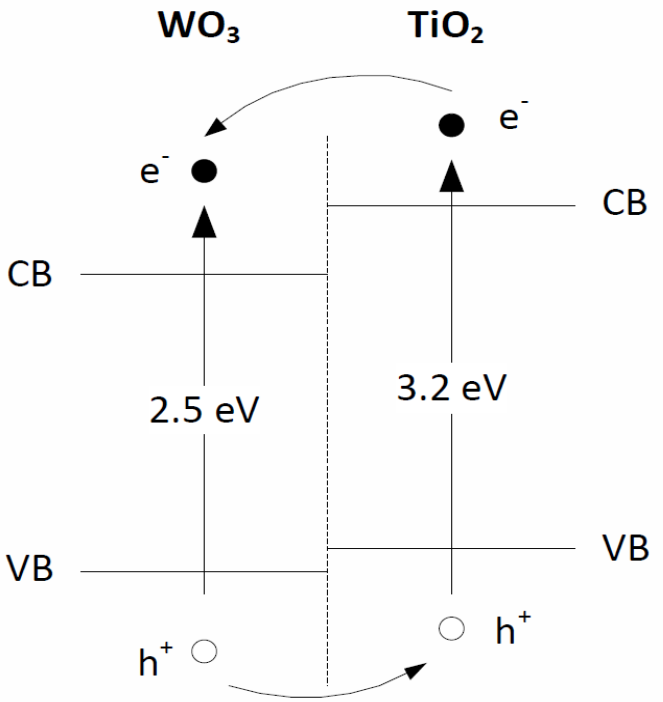


*Fl light activities normalised to same integrated power flux as UV light source

Optimising Dopant Levels: W-doped coatings (PDC/annealed)



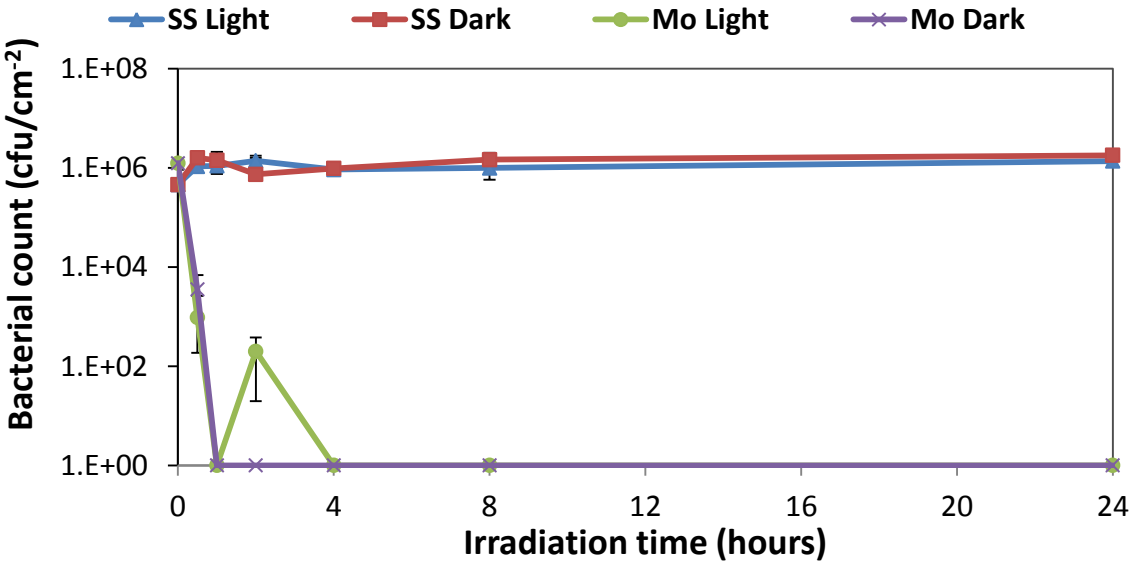
Annealed at 600°C



Lorret, O.; Francová, D.; Waldner, G.; Stelzer, N., *Applied Catalysis B: Environmental* **2009,** *91*, 39-46.

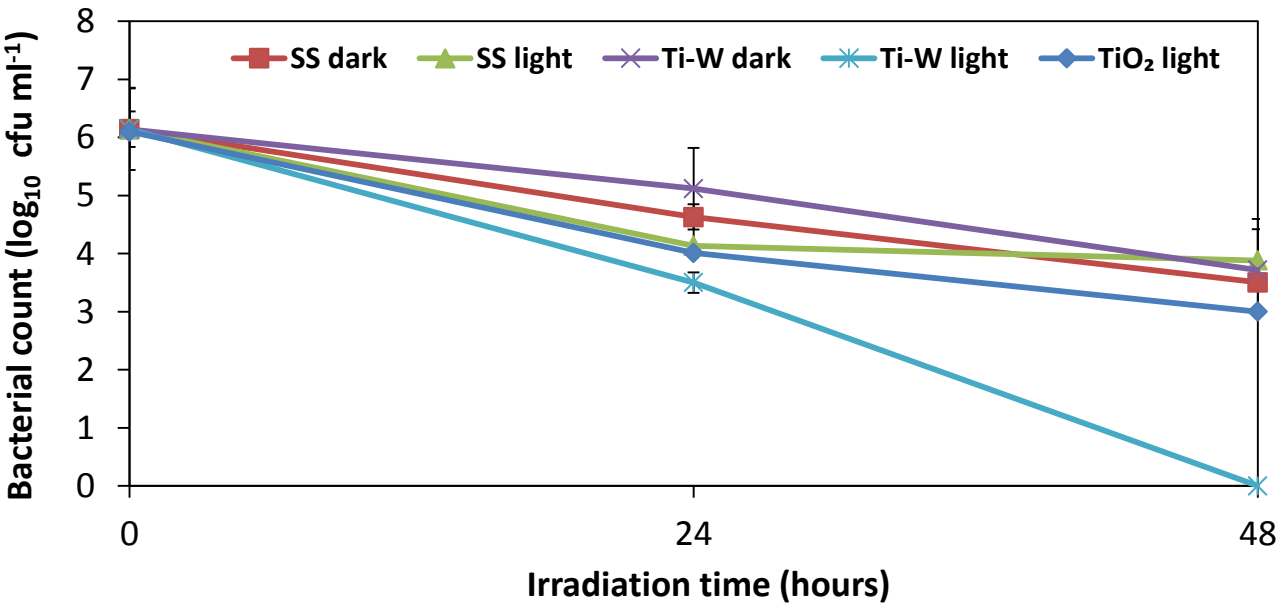
M Ratova, G West, P Kelly, *Coatings* 3 (2013) 194-207.

Antimicrobial effect of doped TiO_2: Fluorescent light



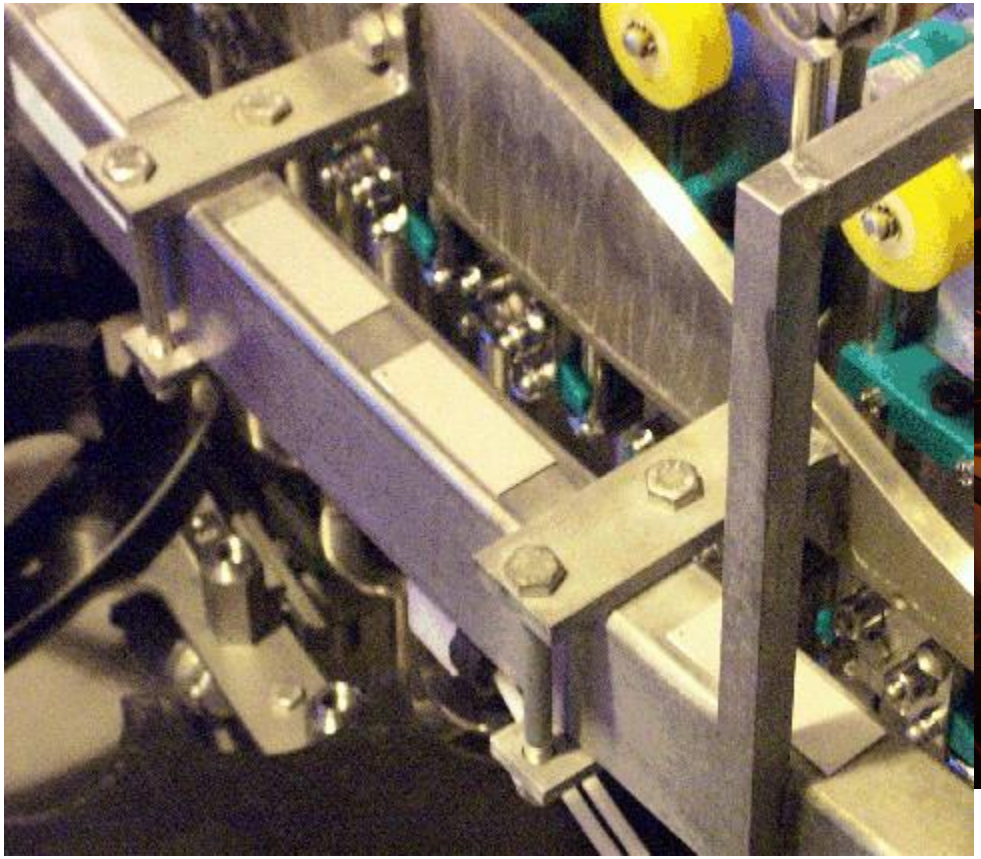
Mo-doped Escherichia coli

***W-doped Escherichia coli*.**



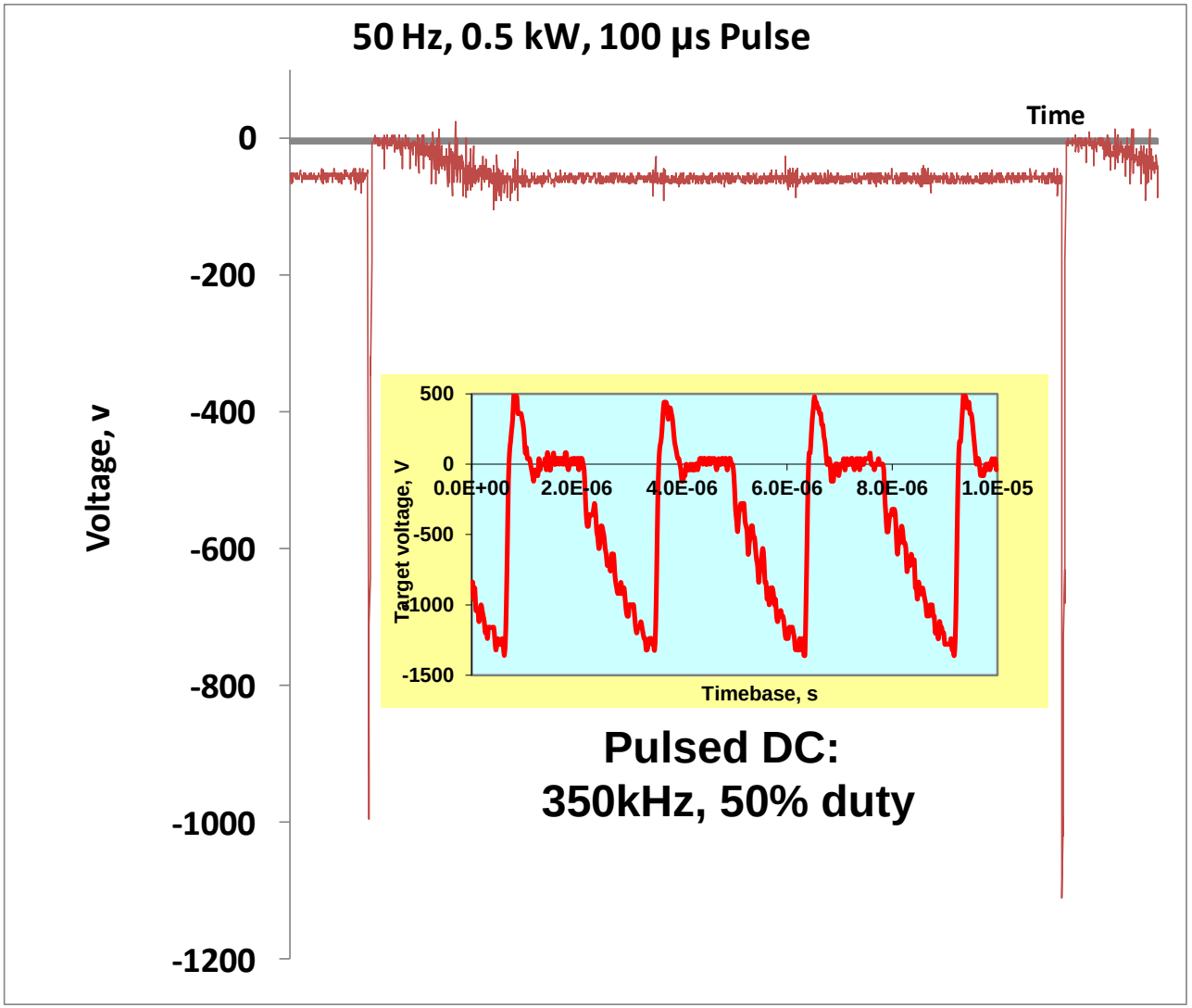
Potential Applications:
Beer bottle filling lines

In collaboration with Panimolaboratorio - Bryggerilaboratorium Ab (PBL), a company devoted to research and development in malting and brewing on behalf of Finnish industry



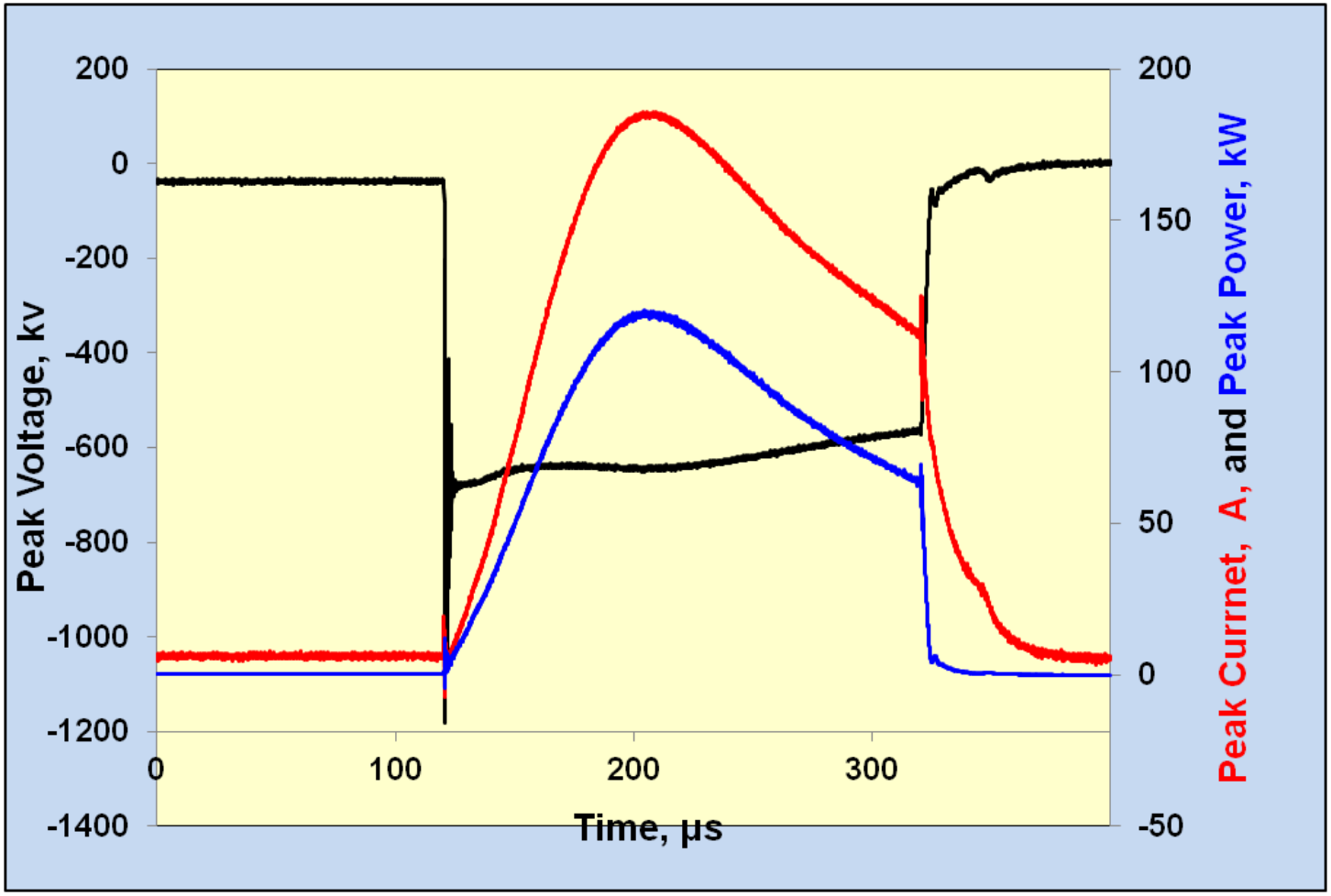
Acknowledgement: Kaisa Tapani, PBL

New Development:
HiPIMS (high power impulse magnetron sputtering)



Peak currents can be 1000A, peak powers can be in MW range
50 – 1000 Hz, 100 – 200 µs pulses, duty 1-10%

New Development:
HiPIMS (high power impulse magnetron sputtering)



HiPIMS may offer the opportunity to produce optimum structures/properties without substrate heating/post deposition annealing

Deposition of Photocatalytic TiO_2 onto PET using HiPIMS

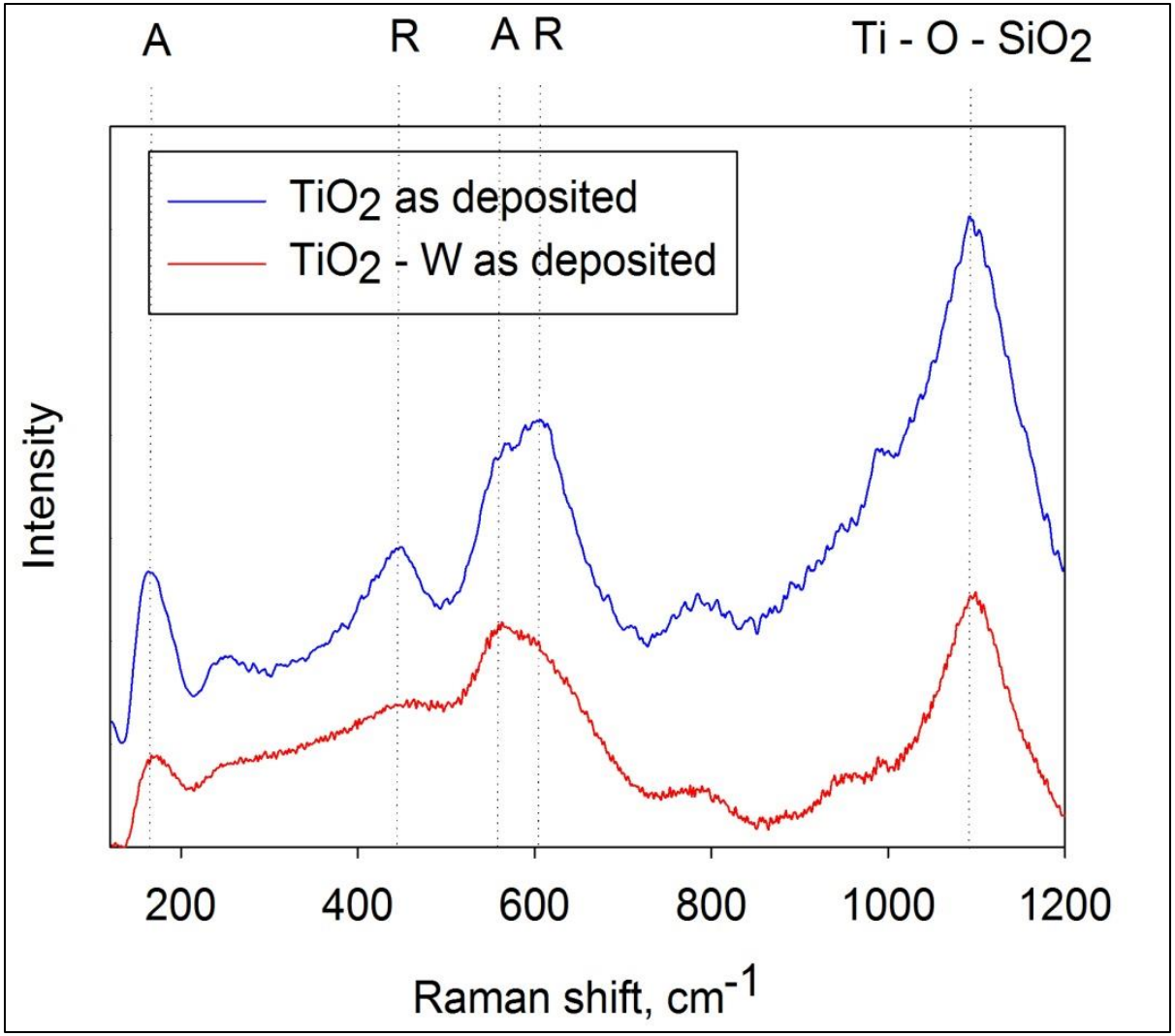
Pulsed DC
100kHz, 50% duty
1.5 kW ave. power

HIPIMS Huettinger
200Hz, 200 μs pulse
1.5 kW ave. power

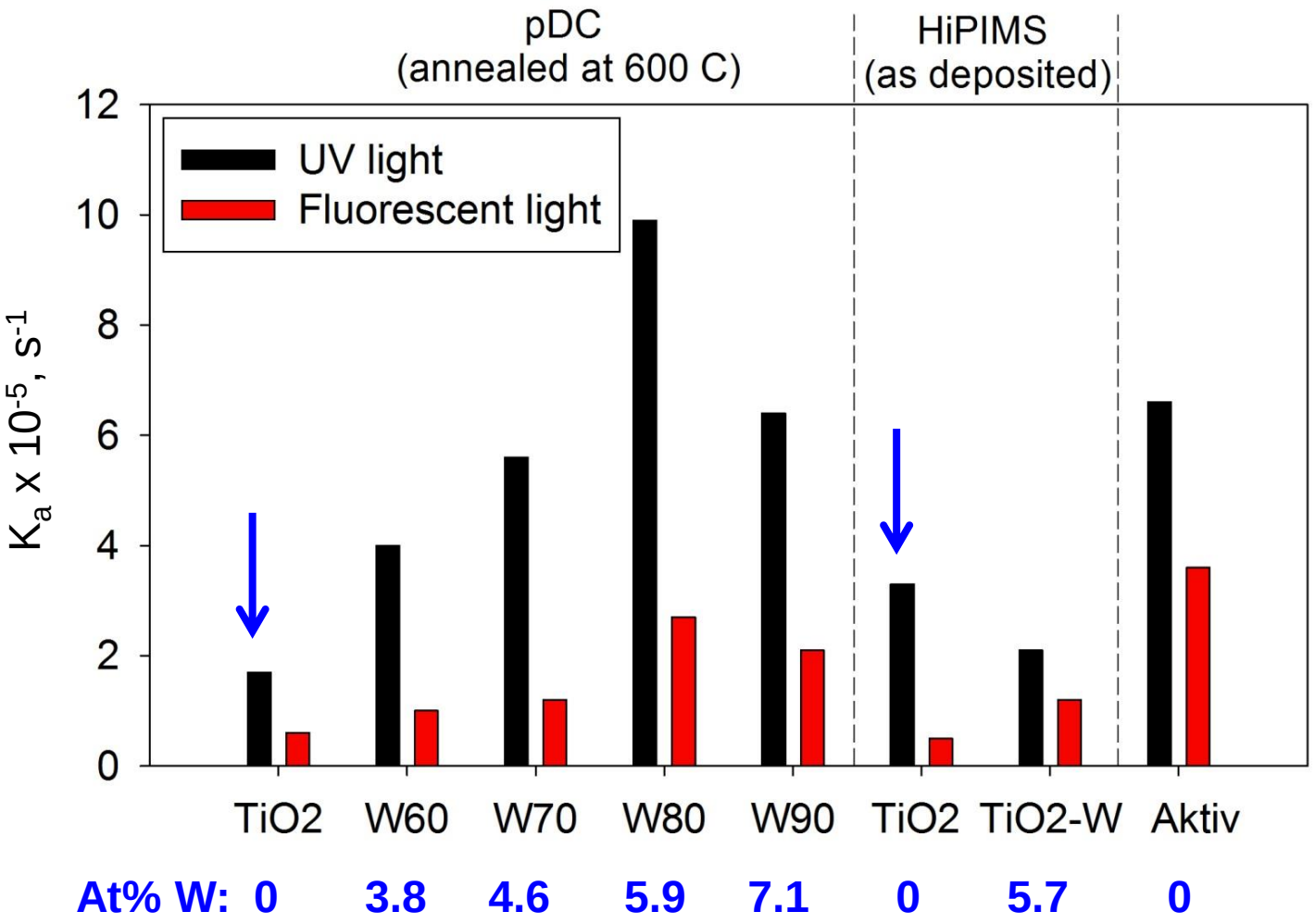
100nm of TiO_2 deposited onto 100μm of PET at same time-average power

GT West, PJ Kelly, P Barker, A Mishra and JW Bradley, *Plasma Process. Polym*, **6** (2009) S543-S547

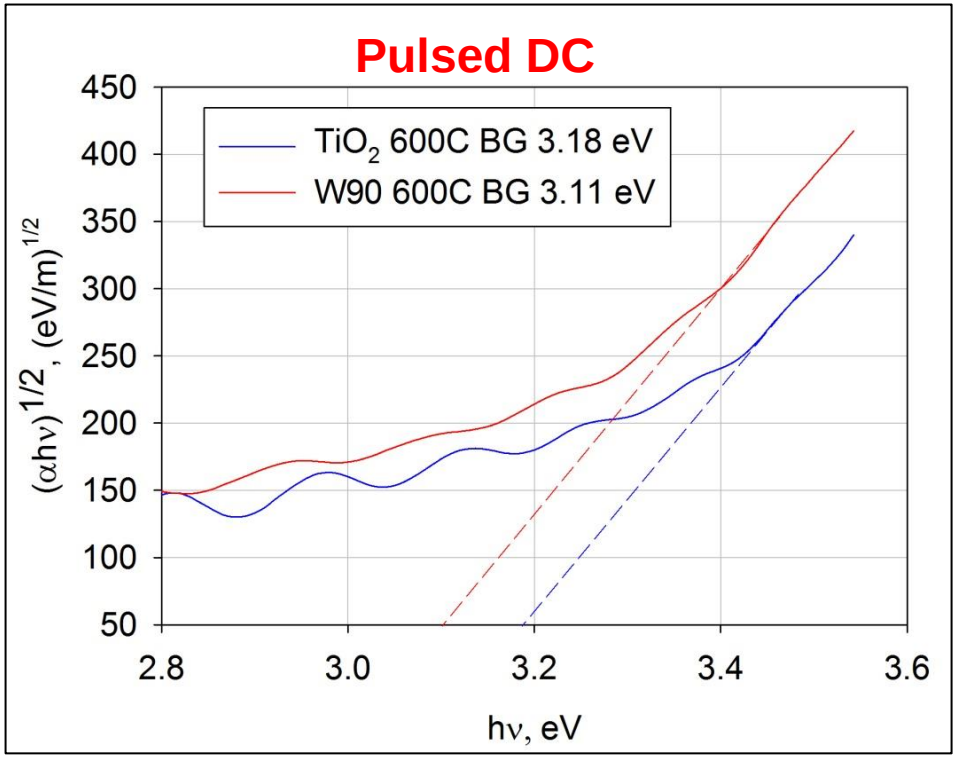
Raman Spectroscopy Analysis of HiPIMS Titania Coatings

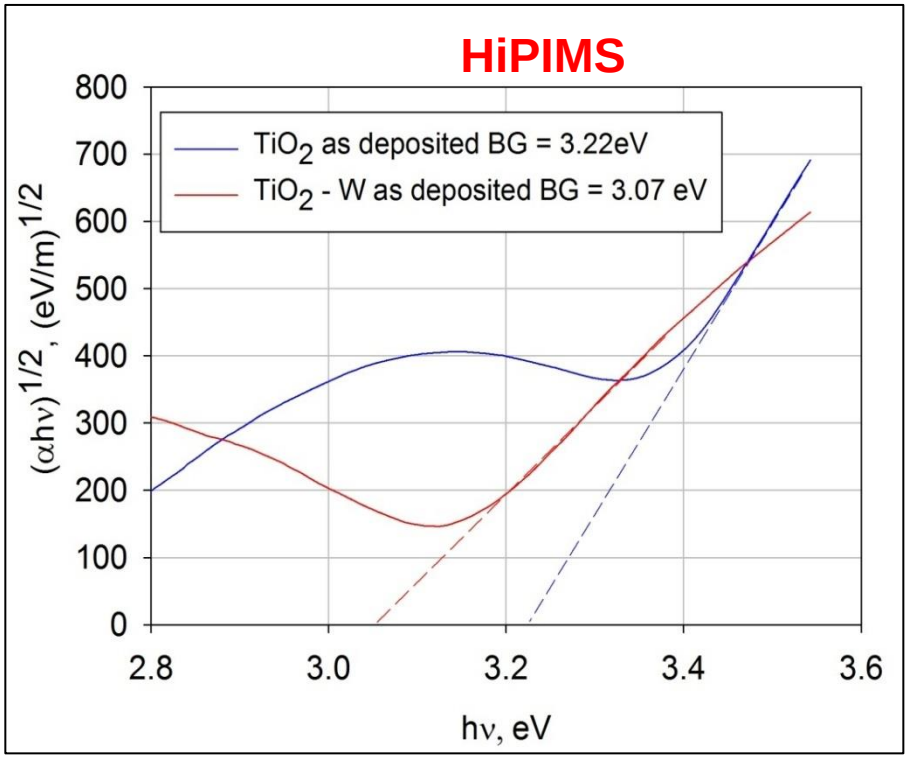


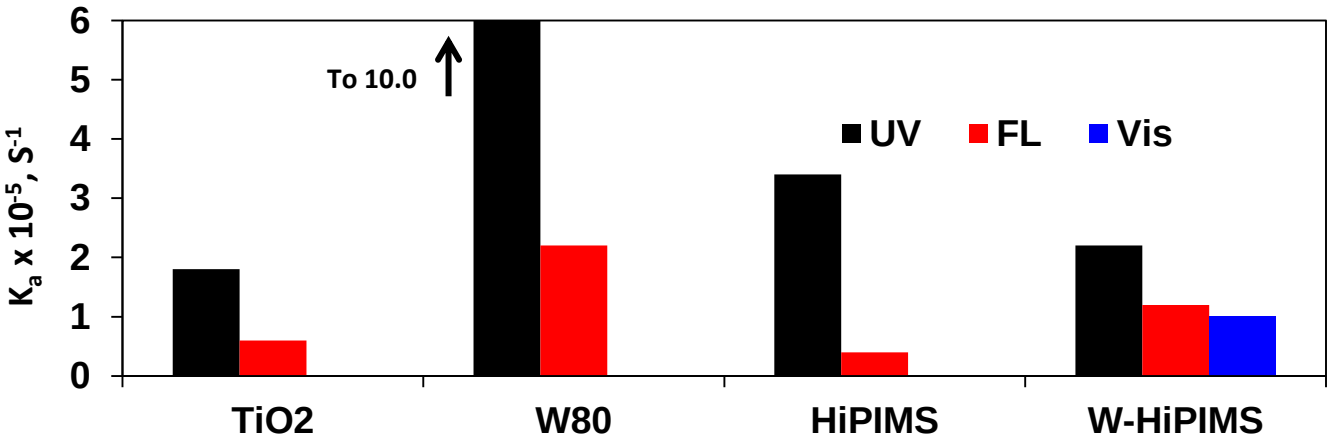
Photocatalytic Results: PDC & HiPIMS



Band Gap Measurements: Tauc Plots

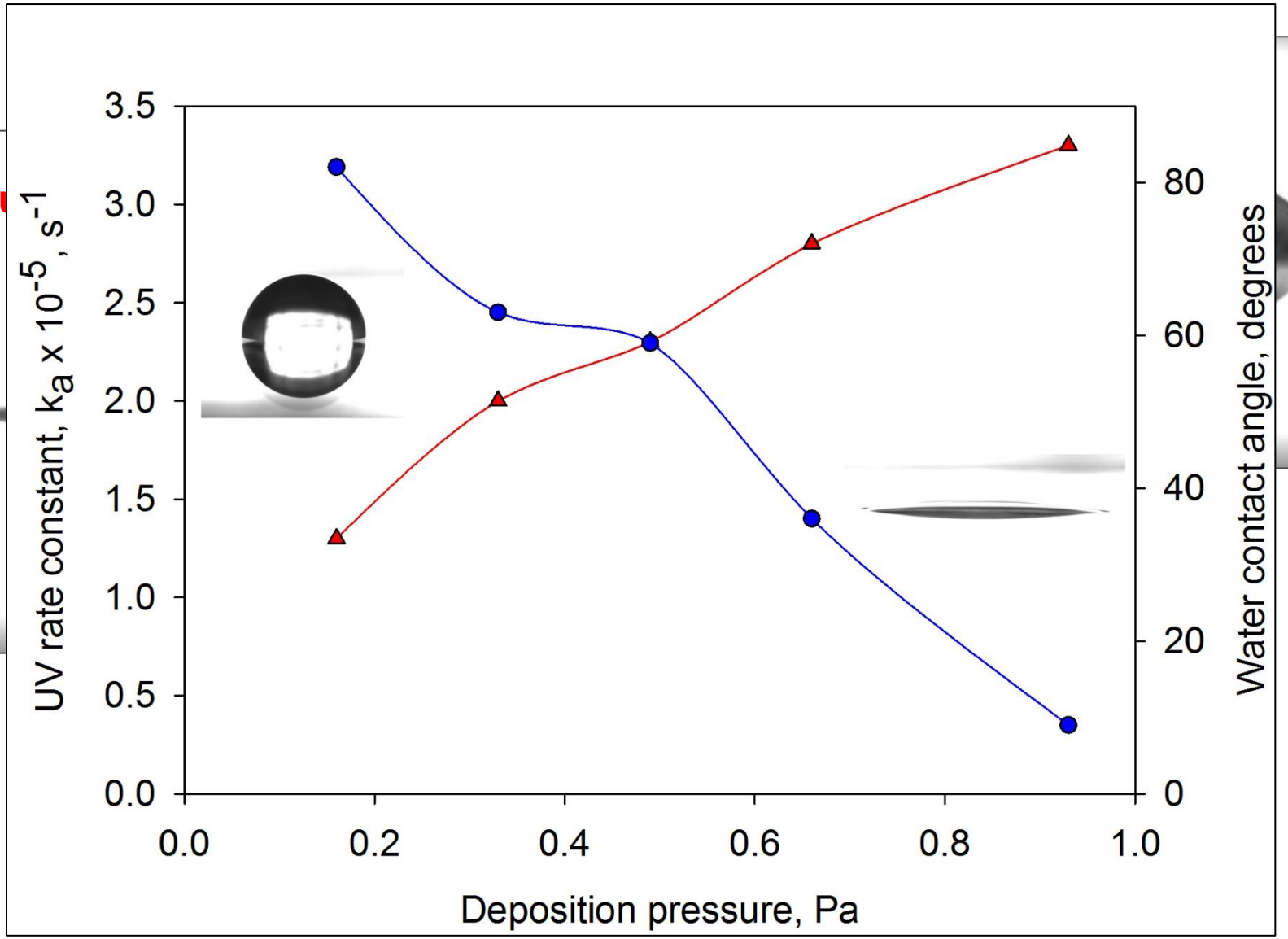






M Ratova, G West, PJ Kelly, 'HiPIMS Deposition of Tungsten-doped Titania Coatings for Photocatalytic Applications', *Vacuum* **102** (2014) 48-50

Water Contact Angle

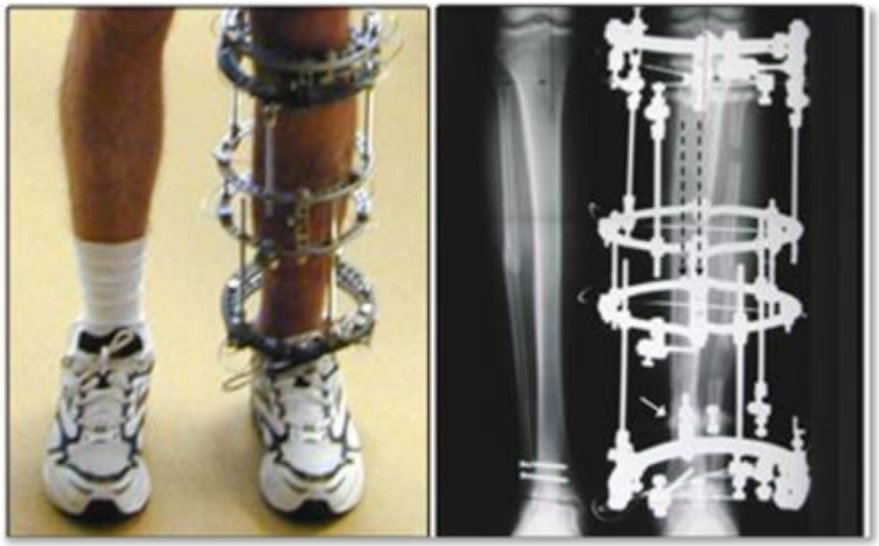


Case Study 1: Summarising Comments

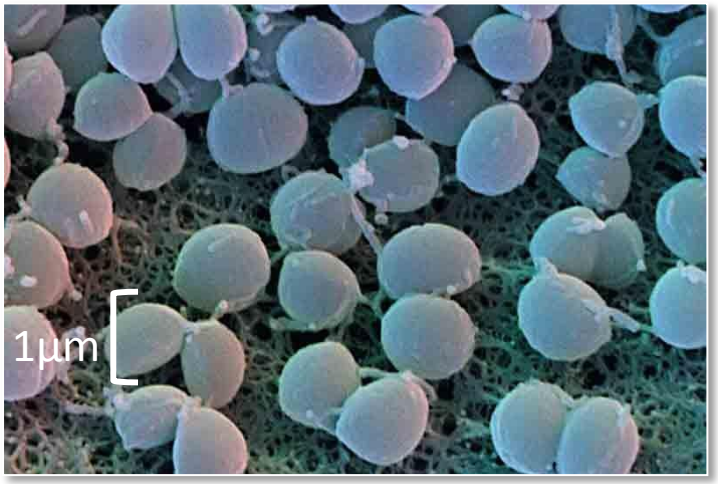
- **Photocatalytic doped-titania coatings have been produced by magnetron sputtering techniques**
  - **Performance assessed in terms of dye degradation, antimicrobial assays, band gap shifts and contact angle measurements**
  - **Wide variation in results**
- **Performance is sensitive to:**
  - **Dopant material and content (Mo and W most active)**
  - **Crystalline structure (annealing temp/dep'n process)**
- **Alternative materials for visible light activity (Bi complex oxides)**
- **Many potential industrial/medical applications**
  - **Bottling line trials underway**
  - **HiPIMS allows single stage processing on polymeric substrates**
  - **Ability to deposit active coatings at low temps opens up new opportunities**

PJ Kelly, et al, 'Structural formation and photocatalytic activity of magnetron sputtered titania and doped-titania coatings', *Molecules,* **19** (2014) 16327-16348.

Case Study 2: Comparison of Tribological and Anti-Microbial Properties of CrN/Ag, ZrN/Ag, TiN/Ag, and TiN/Cu Nanocomposite Coatings



Staphylococci



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Transition Metal Nitride Coatings

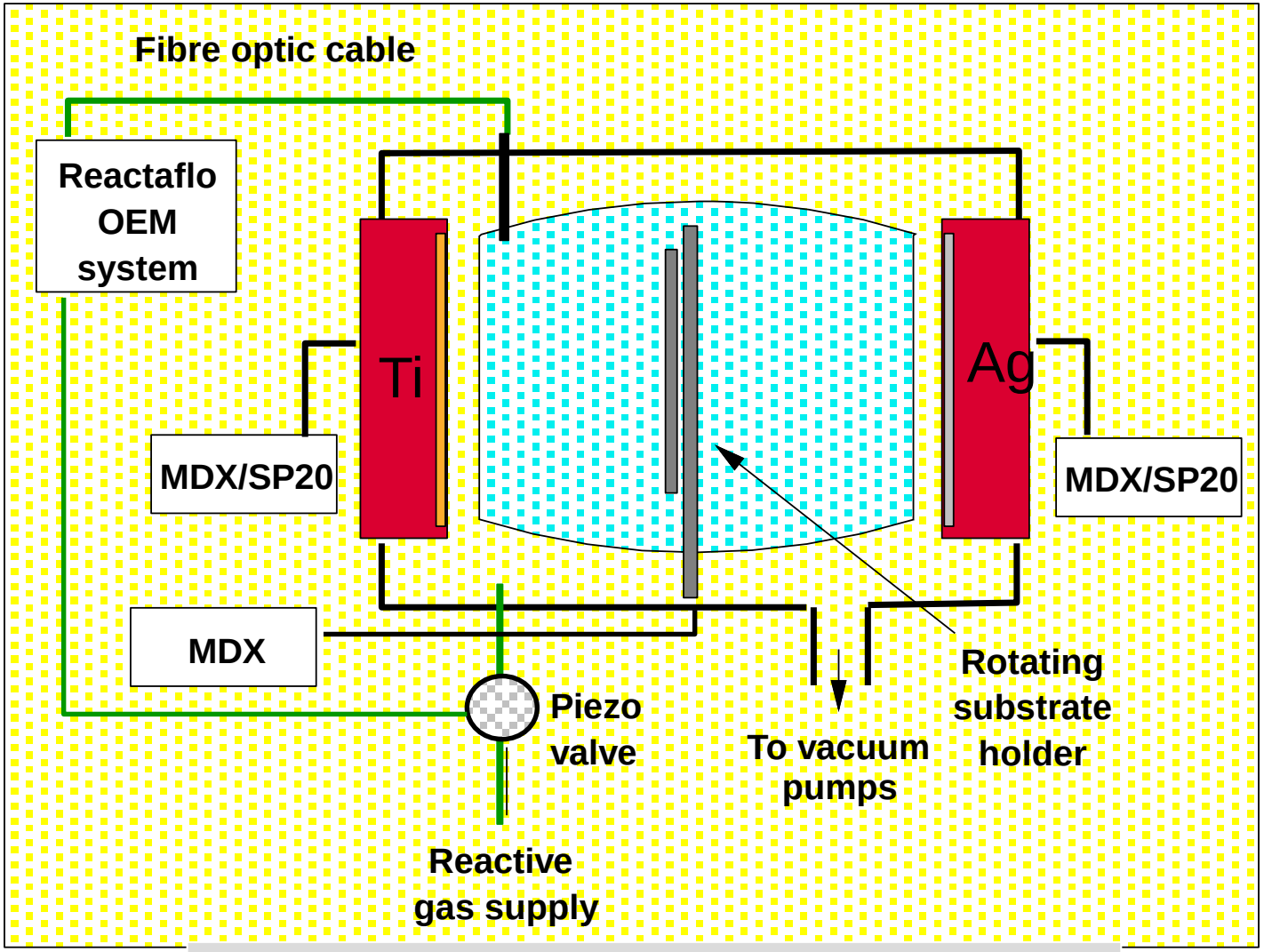
- **TiN, ZrN, CrN, TiAlN, etc.**
- **High hardness, resistance to corrosion and wear and attractive appearance**
- **Industrial applications**
  - **Protection of cutting and forming tools**
  - **Decorative items**

Source: Tecvac


Source: Newform

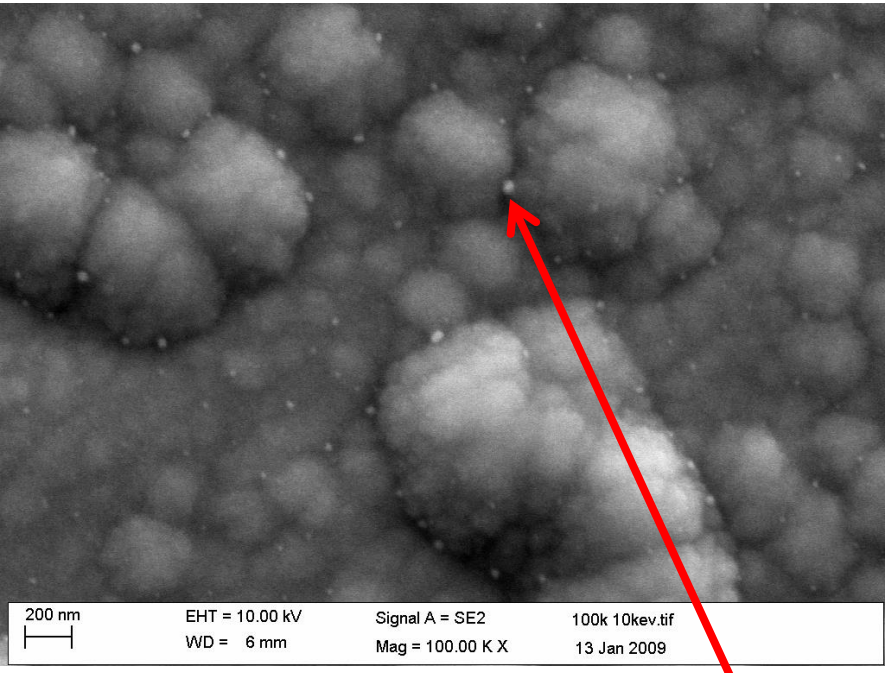

Source: Teer Coatings Ltd

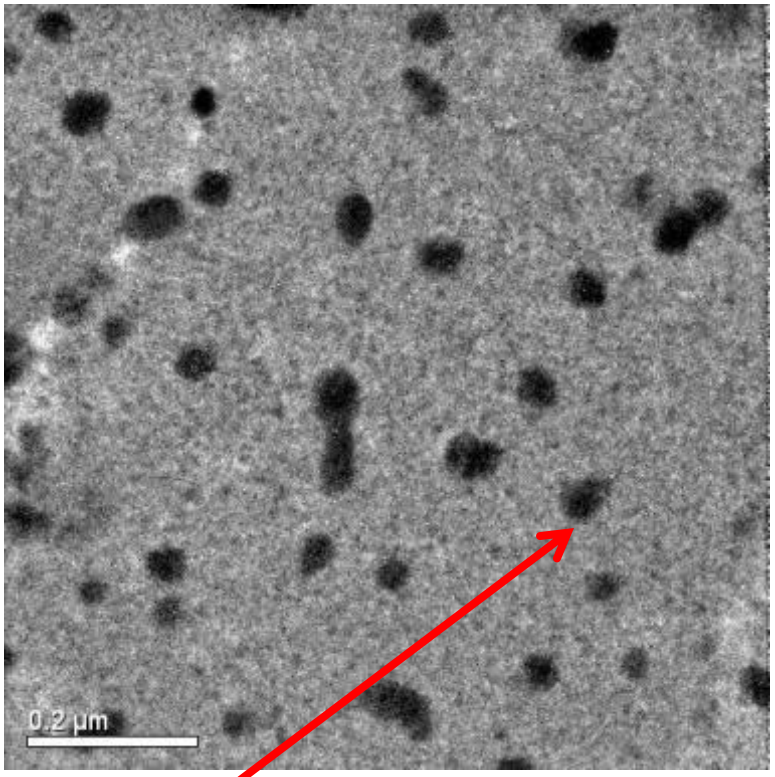
Deposition of TiN/Ag Nanocomposite Coatings



Ti and Ag sputtered simultaneously in Ar/N gas. TiN forms, but AgN is unstable

TiN/Ag Nanocomposite Coatings





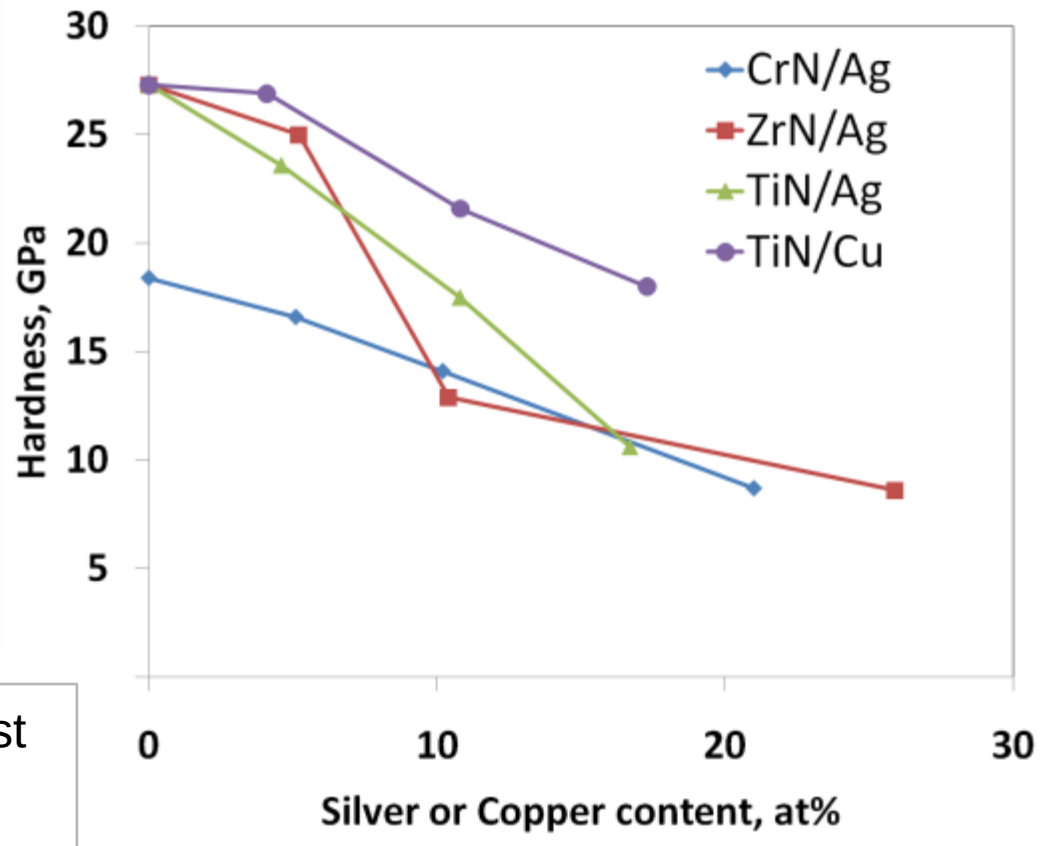
TiN-10at%Ag

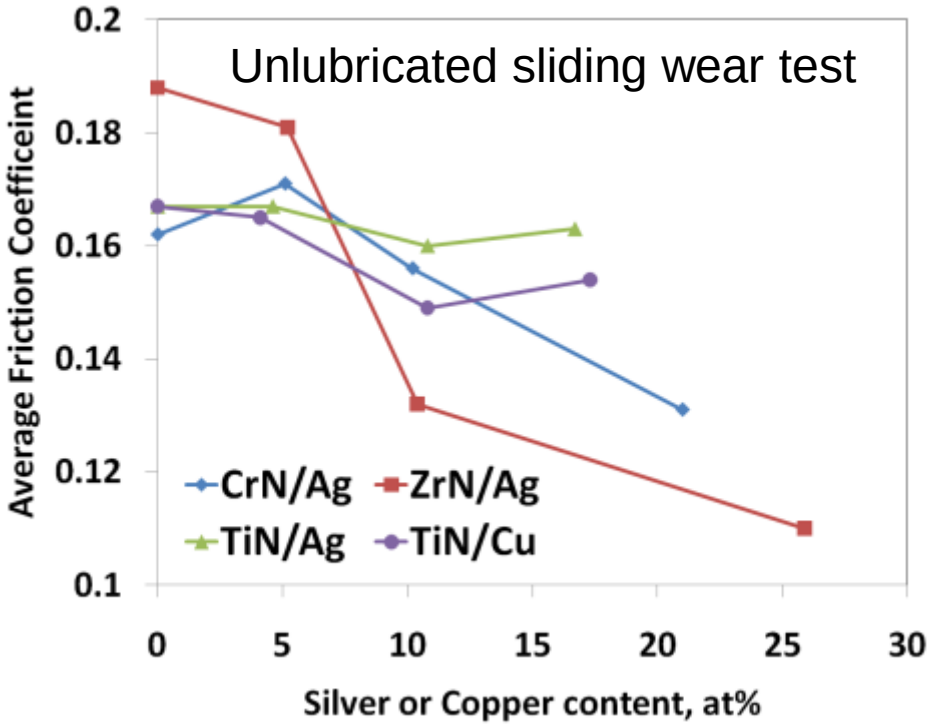
TiN-16at%Ag

Ag nanoparticles

PJ Kelly, et al, 'A Study of the Anti-Microbial and Tribological Properties of TiN/Ag Nanocomposite Coatings', *Surf. Coat. Technol*., **204** (2009) 1137-1140

Coating Properties

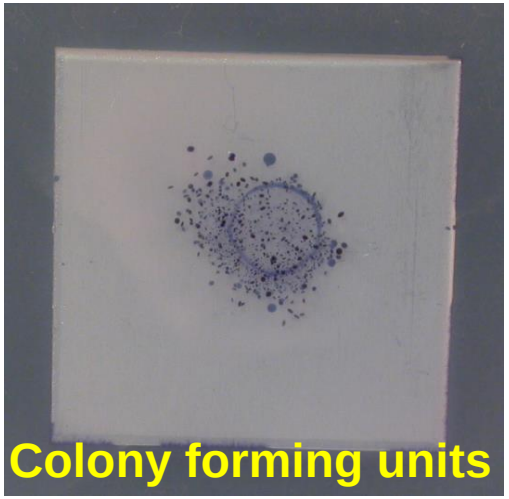


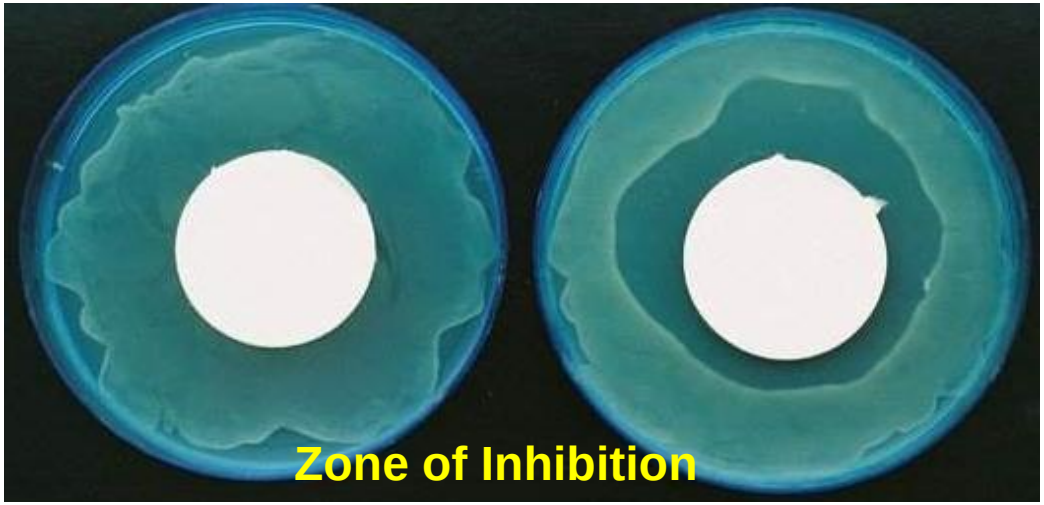


Decreasing hardness and friction with increasing Ag or Cu, but also increasing wear rate

Antimicrobial Activity

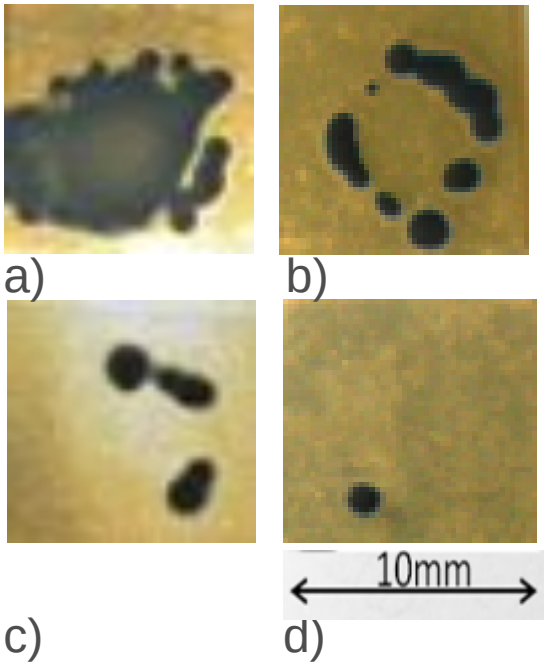
- **Zone of inhibition**
  - **Silver/copper ion release**
- **NBT (nitro-blue tetrazolium) assays**
  - **Contact kill. Tests antimicrobial effectiveness after incubation**
- **Bacteria used:**
  - ***Pseudomonas aeruginosa* (*P. aeruginosa,* a gram negative rod shaped bacterium with flagellum),**
  - ***Staphylococcus aureus* (*S. aureus*, a gram positive 1 µm diameter coccal bacterium)**

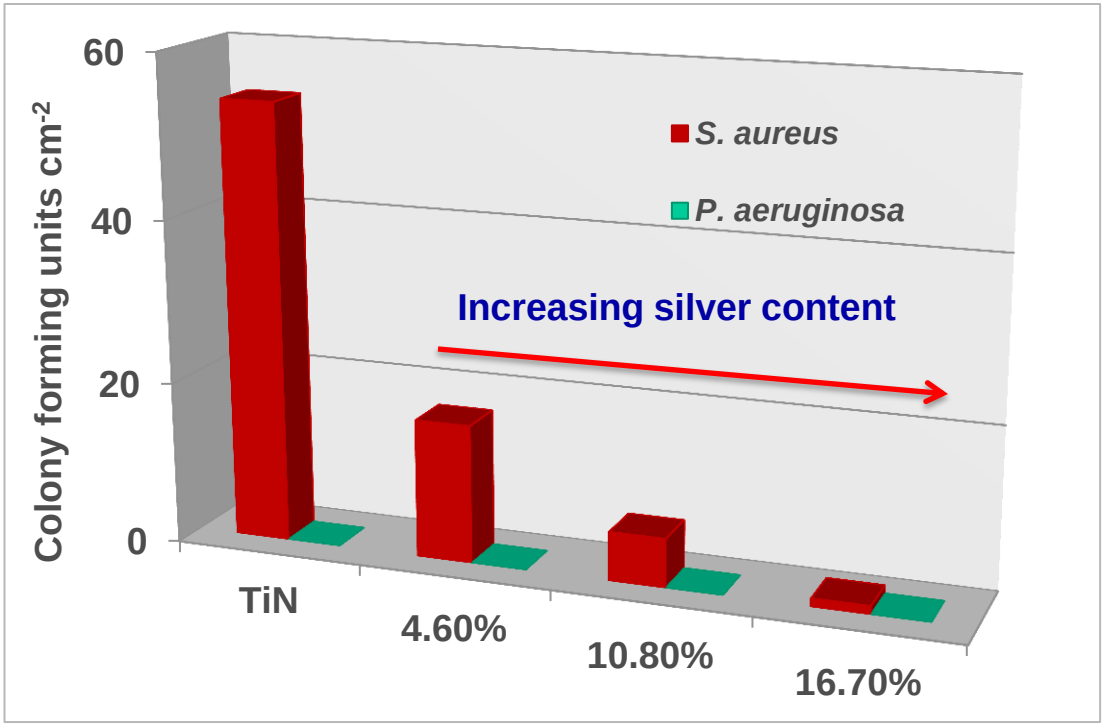




Microbiology Results: *Staphylococcus aureus*

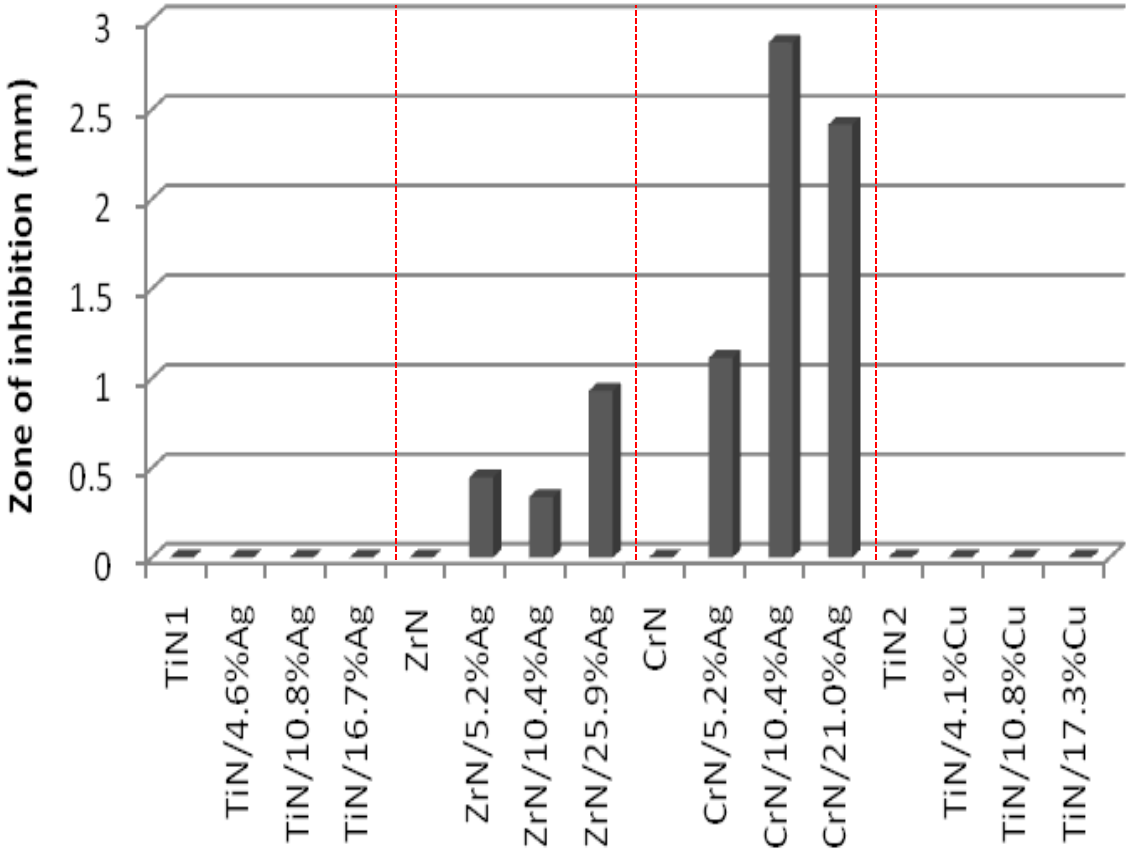
- **No ZOI observed (zone of inhibition)**
- **For NBT assays, *S. aureus* colonies were present on all the surfaces, but the number of colony forming units decreased significantly with increasing silver content.**

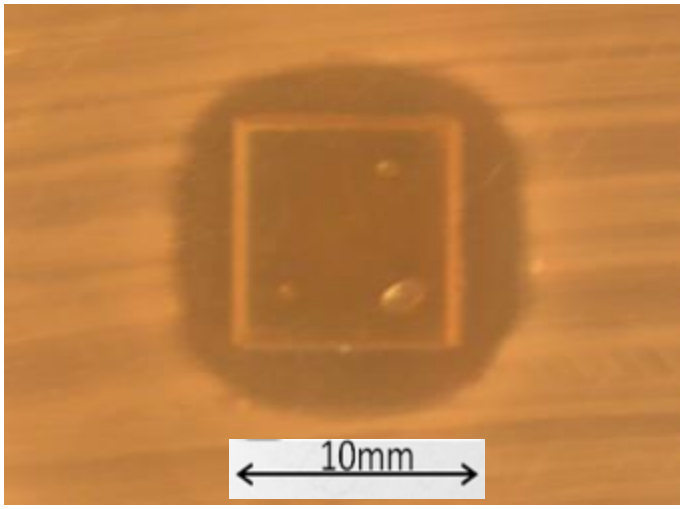




a: TiN; b:4.6% Ag;
c: 10.8% Ag,; d: 16.7% Ag

ZoI – All Coatings
Pseudomonas aeruginosa





ZoI surrounding CrN/10.2%Ag against *P. aeruginosa* cells

Case Study 2: Summary

- **Nanocomposite transition metal nitride coatings have been produced with varying Ag and Cu contents**
  - **Decreased friction coefficients in wear tests**
  - **Also decreased hardness and increased wear rates**
- **Coatings can combine enhanced tribological properties with antimicrobial activity, but results are coating and organism specific**

PJ Kelly, et al, 'Comparison of Tribological and Anti-Microbial Properties of CrN/Ag, ZrN/Ag, TiN/Ag, and TiN/Cu Nanocomposite Coatings,' *Surf. Coat. Technol*., **205** (2010) 1606-1610

Conclusions

- PVD processes are extremely versatile and successful
- Magnetron sputtering now process of choice in many cases
- Continuous development over ~20 years has provided improvements in properties/process
  - Unbalanced magnetrons
  - Closed field multiple magnetron systems
  - Pulsed magnetron sputtering
  - HiPIMS
- Applications of magnetron sputtering will continue to grow
  - Versatility
  - Reliability
  - Scaleability
  - Clean process