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Advances In Thermochromic Thin Films

Dr Russell Binions

The Challenge

What should we aim for?

Some observations

CVD, EACVD – some results

How did we do?

What did we learn?

The Challenges!

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Increasing number of glass fronted buildings being built

Traditional insulation methods are not applicable

Increasing use of heating and air conditioning

Bigger CO_2 footprint

Higher Energy Bills

Energy Efficient Glazing will help Reduce our Emissions & save us Money!

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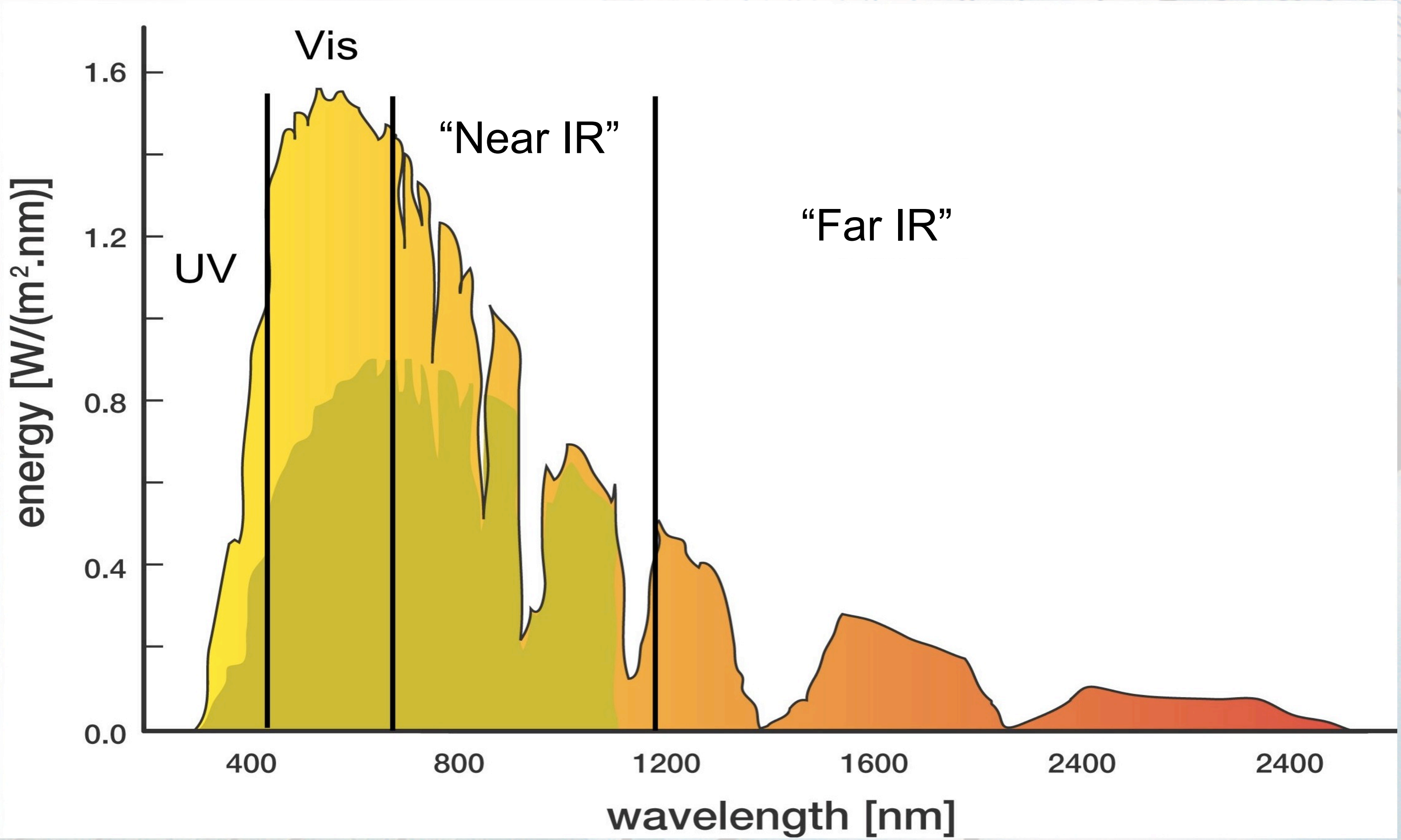

Solar Control / Heat Mirrors –

Strongly reflect in near IR.

Prevents solar energy entering a building.

Typically sputter coated very thin films of metal such as silver.

Low Emissivity (Low E) –

Such as K-glass.

High reflectivity in far IR.

Prevents blackbody radiation escaping.

Absorbing Glass –

Coloured.

Absorbs in near IR.

Prevents solar energy entering a building.

8 July 2013 Last updated at 14:47

Share

Green Deal 'could lead to deadly summer overheating'

By Brian Wheeler
Political reporter, BBC News

Temperatures could soar to dangerously high levels in some homes insulated under the government's flagship Green Deal scheme, experts have warned.

Top floor flats in 1960s tower blocks are particularly at risk from overheating, according to research

Energy-saving measures designed to save on winter fuel bills and protect the environment could pose a risk to health during summer heatwaves, they add.

The government says it is aware of the problem and is taking steps to prevent overheating in Green Deal properties.

Homes in densely populated urban areas such as London are most at risk...

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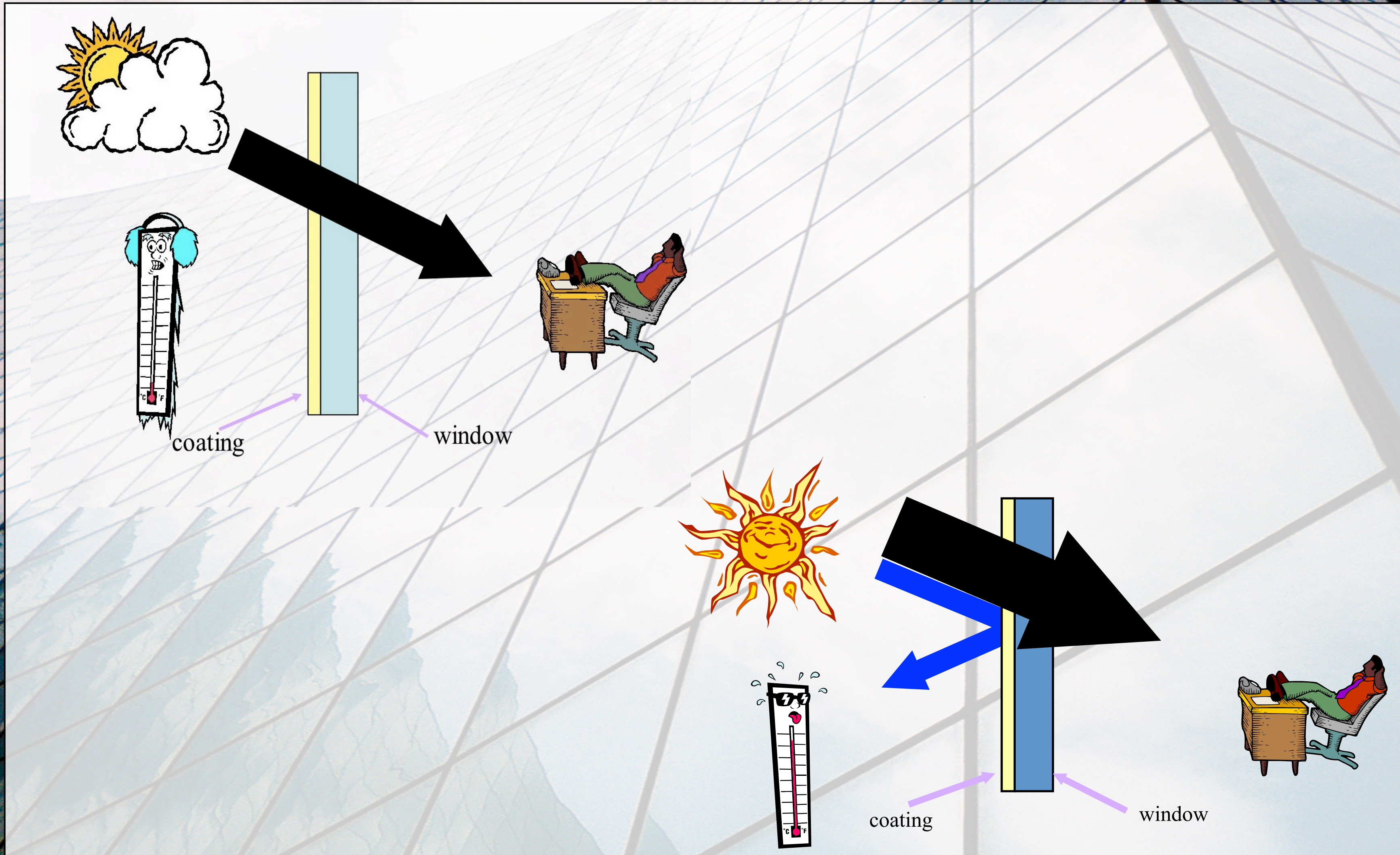
Features

Buzz off
Where have all the wasps gone this summer?

Dragon's legacy
Bruce Lee celebrated 40 years after his death

'A curious person'
Nobel-winning biologist Sir Paul

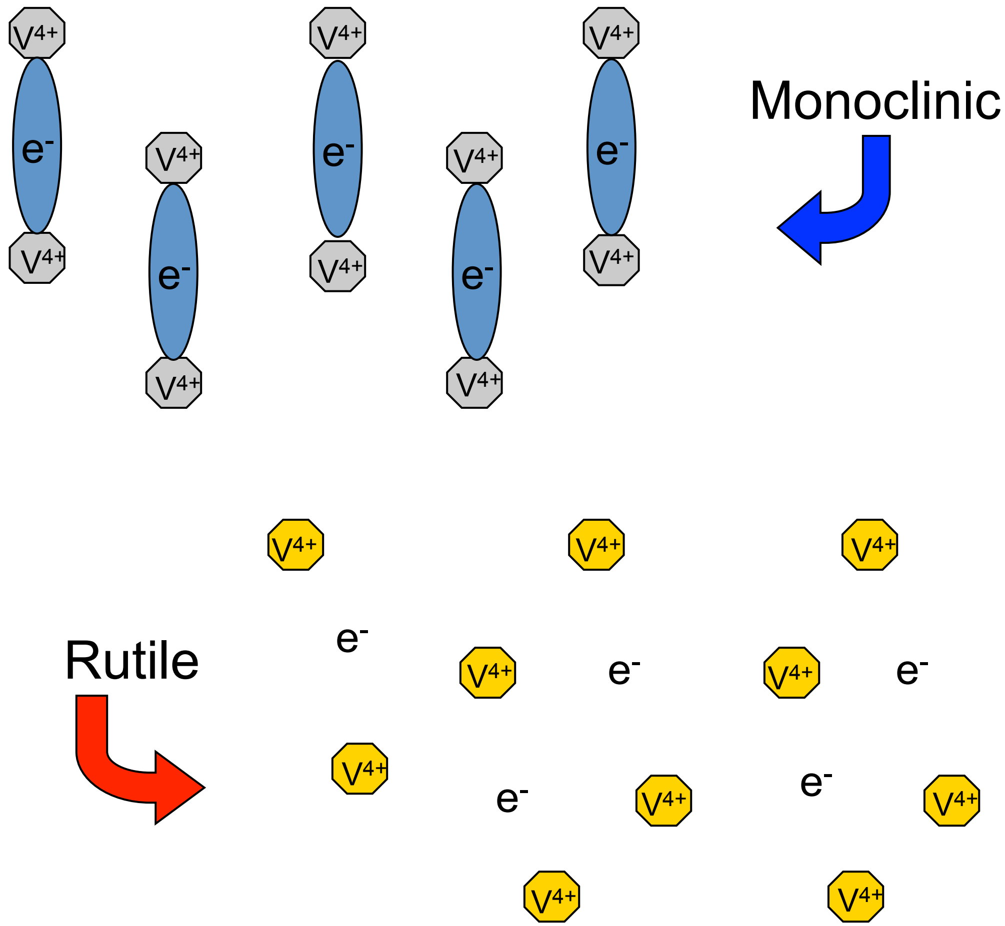

coating
window
coating
window

- Thermochromism in VO_2 is caused by a structural phase change from monoclinic (semiconducting) to rutile (metallic).

- The phase change causes a Disruption of V^{4+} pairs seen in the monoclinic phase.

- This subsequent "freeing" of Electrons leads to metallic behaviour in the high temperature rutile phase.

- This metallic behaviour leads to enhanced IR reflection with negligible change in the visible portion of the spectrum.



Transition Temperature

The ideal transition temperature? Less than 68 ºC (single crystal VO_2)

Metal doping - tungsten, niobium etc.

Film strain / preferential orientation - growth conditions

Particle Size

Thermochromic Efficiency

Hysteresis behaviour (width & gradient) - particle homogenity

Maximising transition in the infrared - ?

Film Colour

Vanadium dioxide is an unappealing brown colour

Nanocomposites - gold nanoparticles

Magnesium or Fluorine doping

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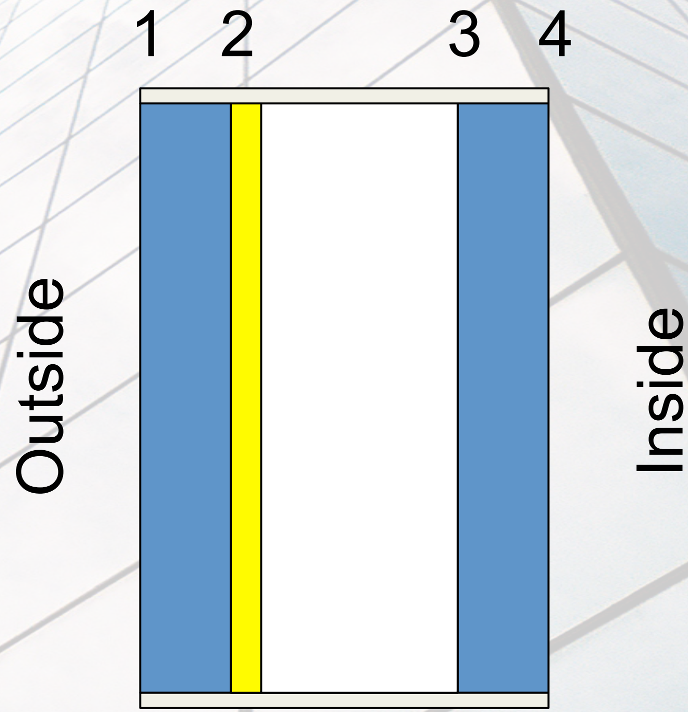
What should we be aiming for?

Double Glazed Window Unit

4 mm float glass

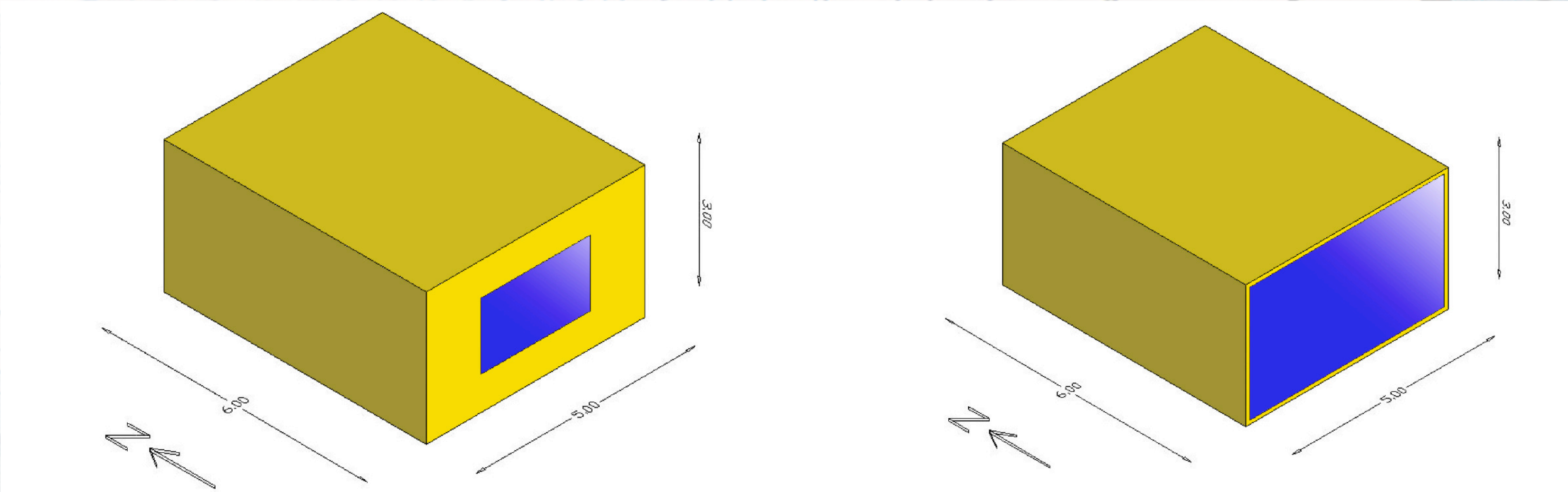
12 mm gap

Film applied on surface 2



Surface temperature on all surfaces calculated – transition temperature based on surface 2 temperature

“Residential” “Commercial”



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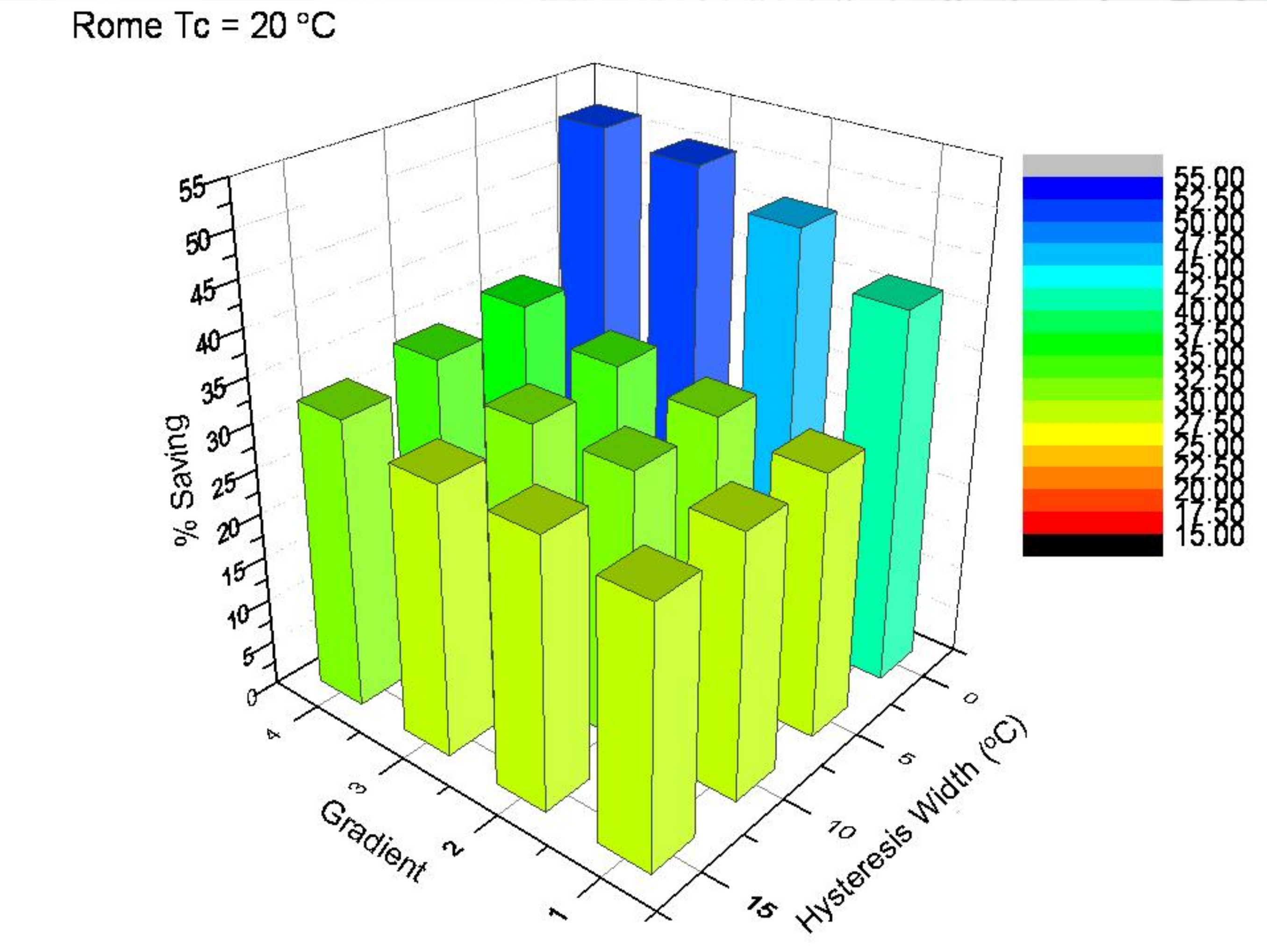
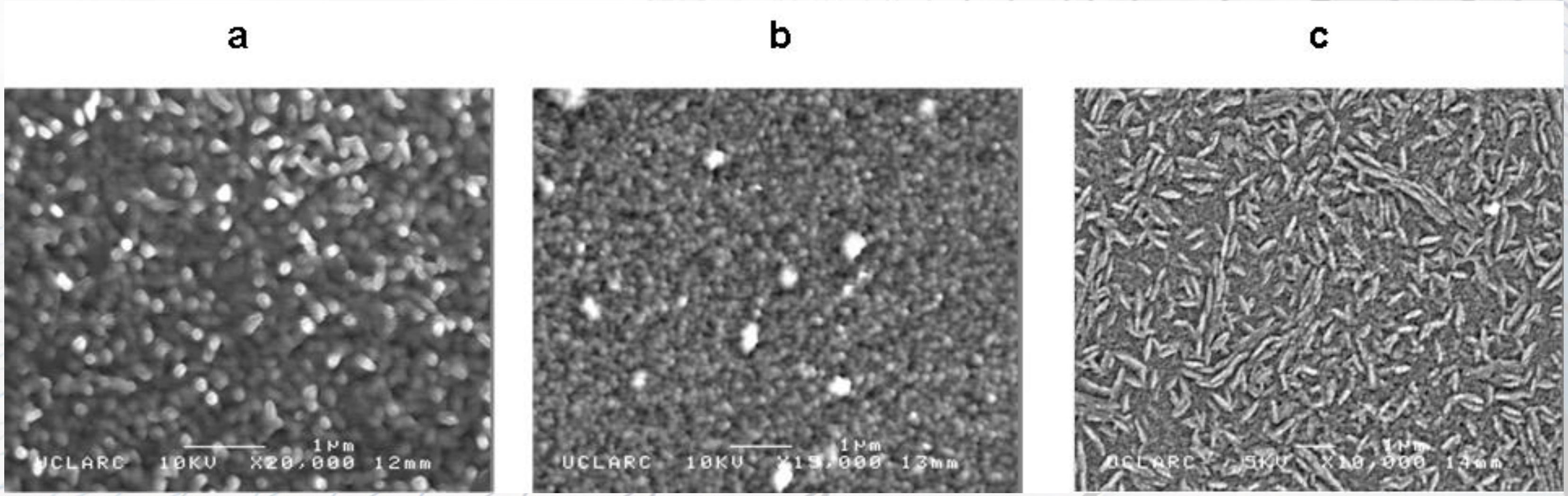
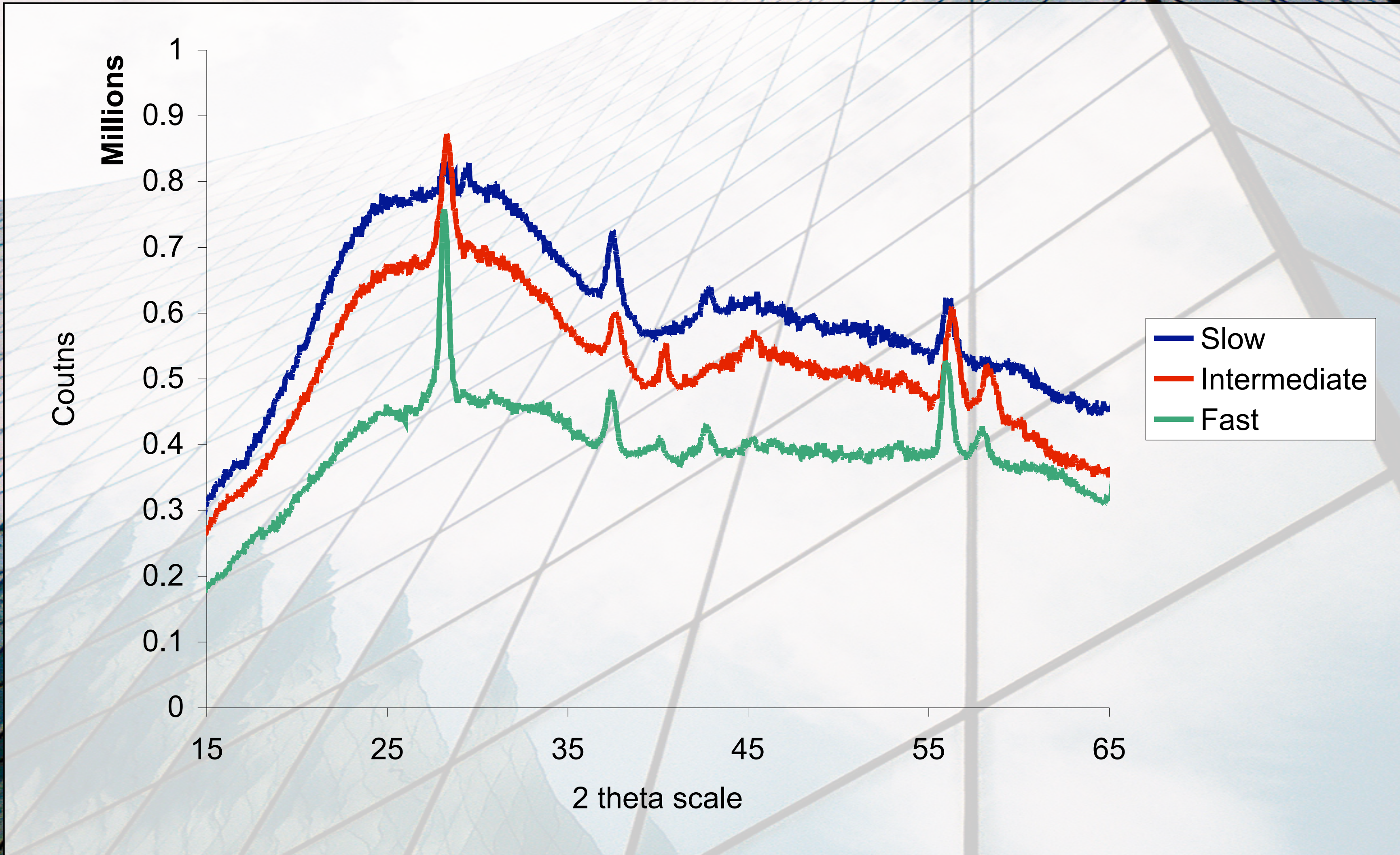


- The ideal thermochromic film will be/have…
- An instantaneous (sharp) transition
- An infinitely narrow hysteresis
- A transition temperature around 20 ºC
- If we can achieve this we might get an additional energy benefit of ~50% compared to double glazing or an additional 10-15 % to existing industry standards (depending on where you live / what your standards are)
- Actually, if we can get close to ideal, the energy benefit will still be significant

Some Observations…



Slow	Intermediate	Fast
10-20 $nm.min^{-1}$	40 $nm.min^{-1}$	150 $nm.min^{-1}$


Millions
Coutns
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
15
25
35
45
55
65
2 theta scale
Slow
Intermediate
Fast

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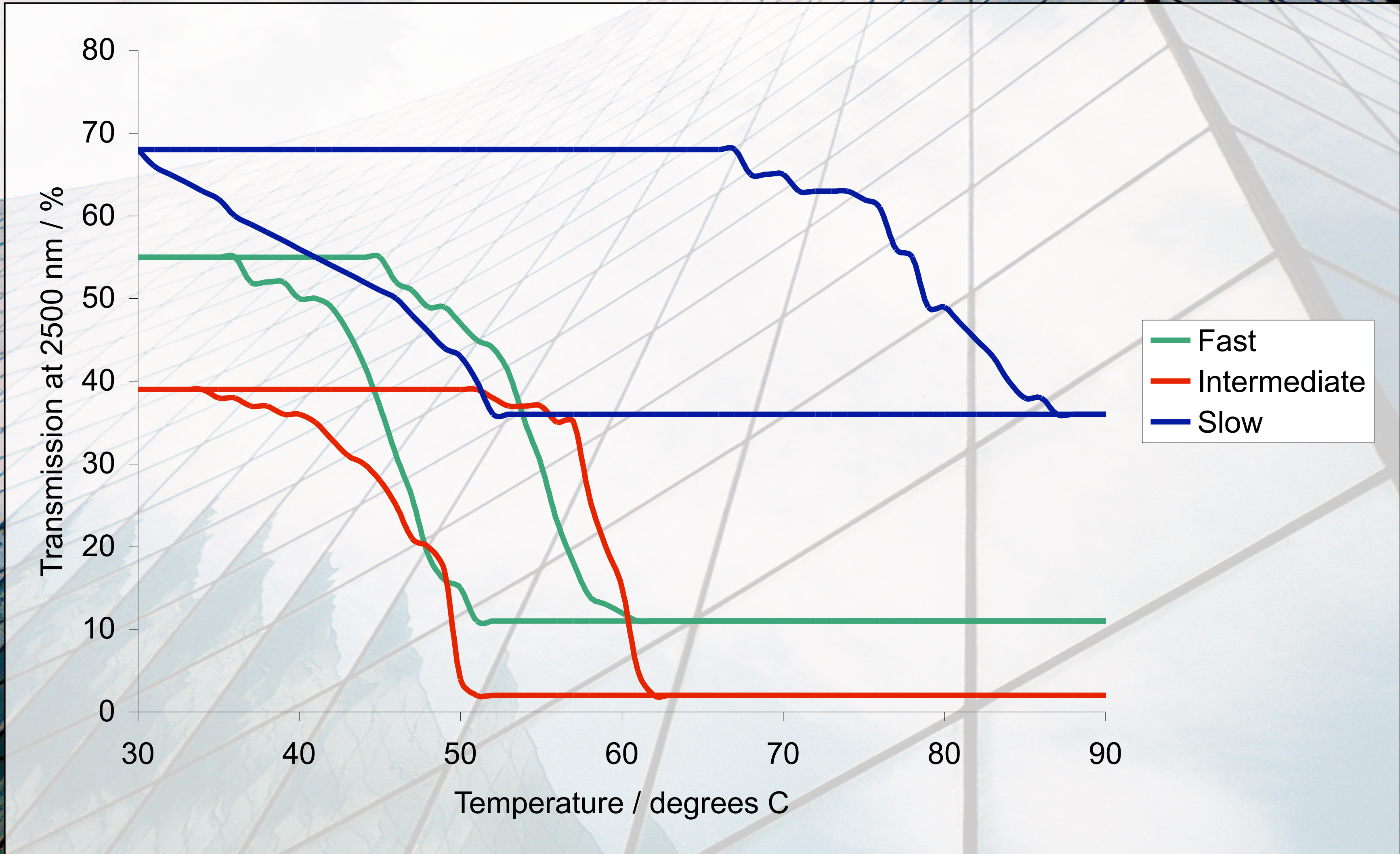


- Take home message is that there is a structure property relationship for thermochromic vanadium dioxide thin films.

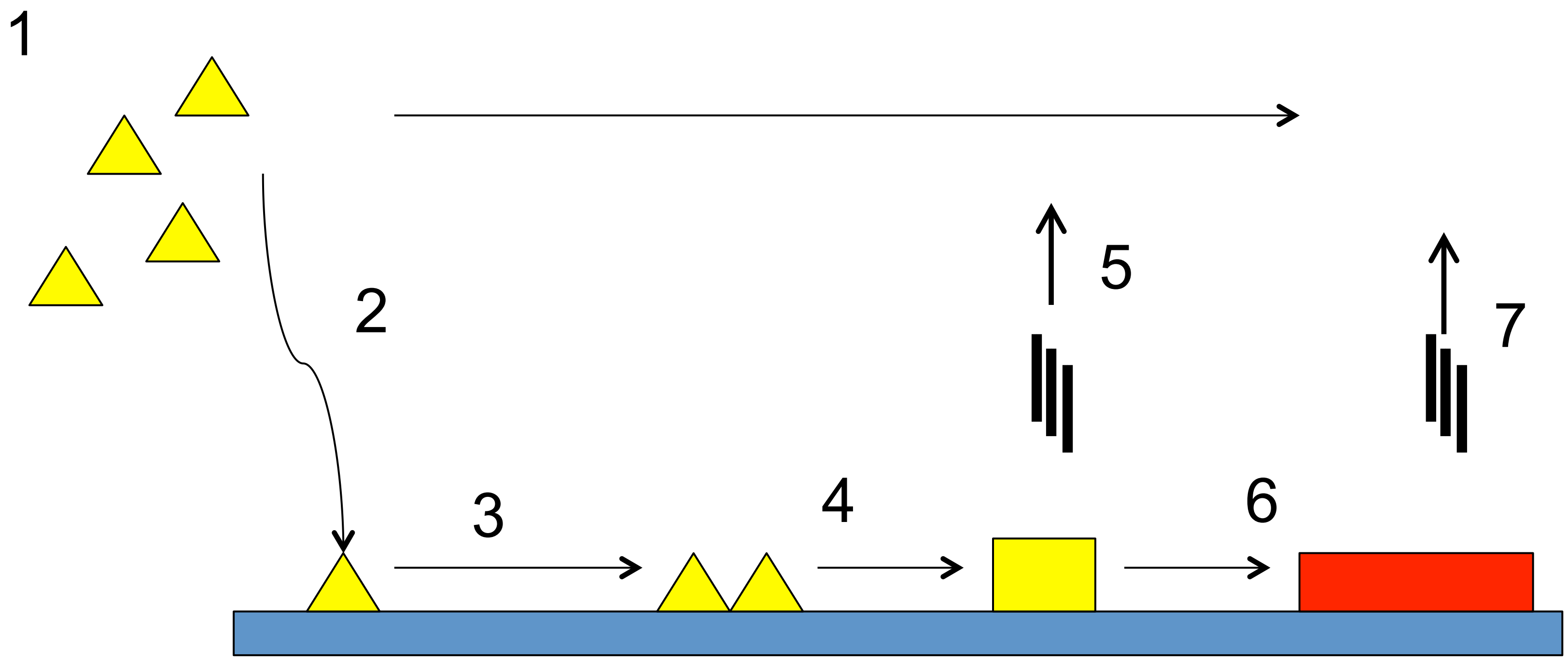
- If we can manipulate film structure enough, we ought to be able to produce films with near ideal properties.

- How can we achieve this?

Electric Field Assisted CVD

Concept

What is Chemical Vapour Deposition?



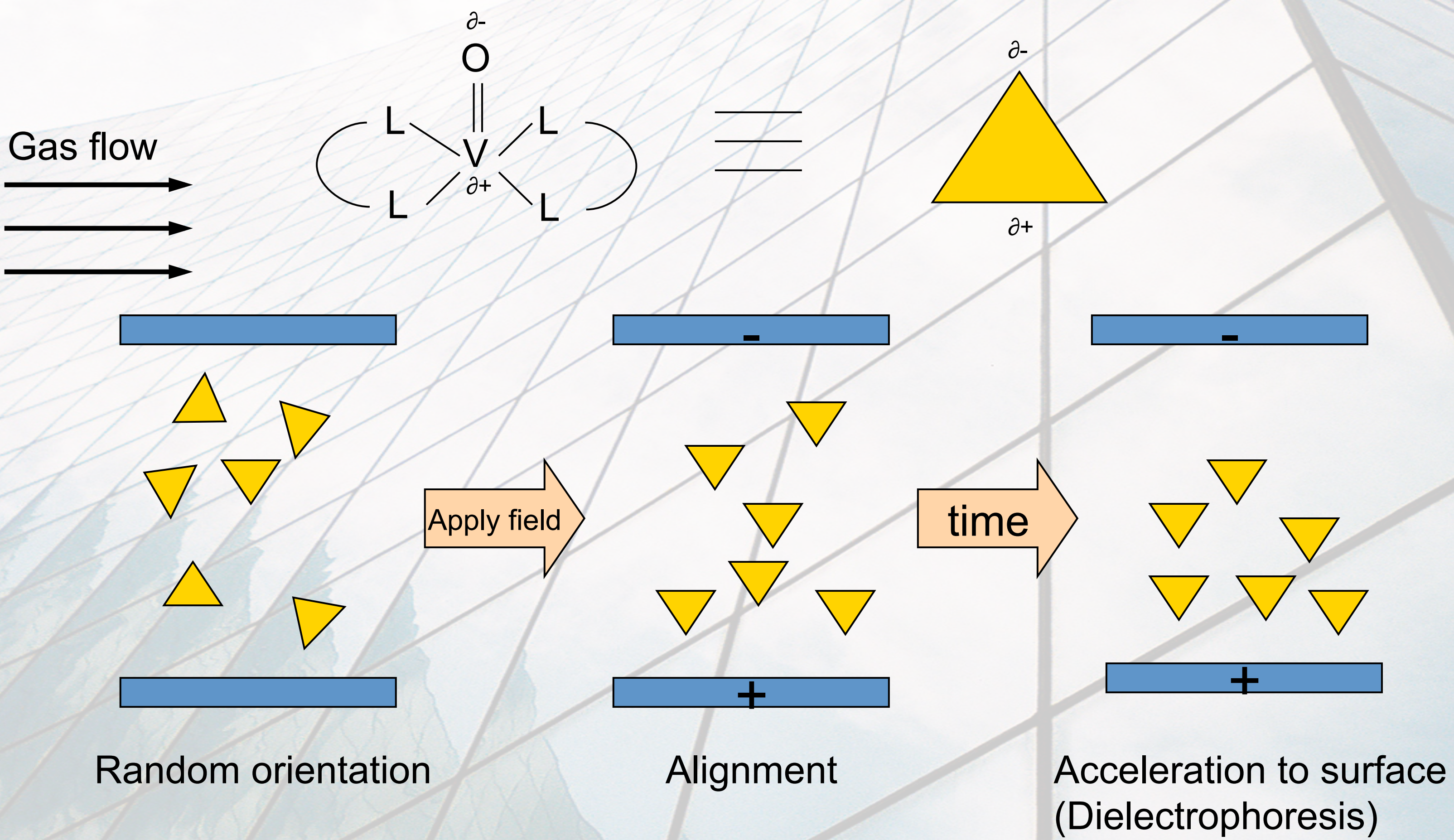
Classical CVD - Ignore gas phase species

Reality - Lots of different gas phase species

At least some of these species have dipoles / charge

An applied electric field should interact with these

Hope to see interesting film growth effects and changes in film properties


Gas flow
∂-
O
L
L
V
∂+
L
L
∂-
∂+
-
-
Apply field
time
+
+
Random orientation
Alignment
Acceleration to surface
(Dielectrophoresis)

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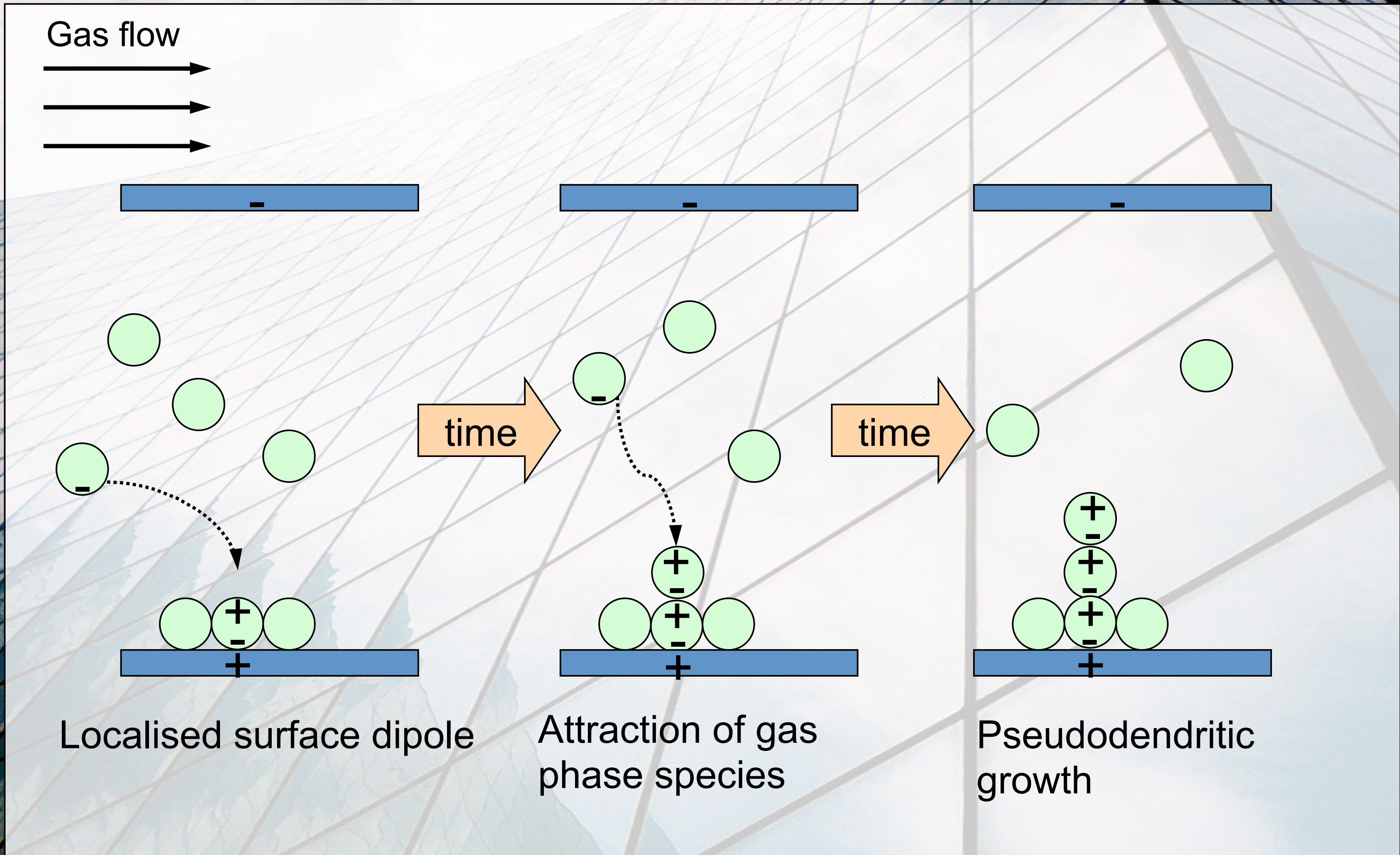
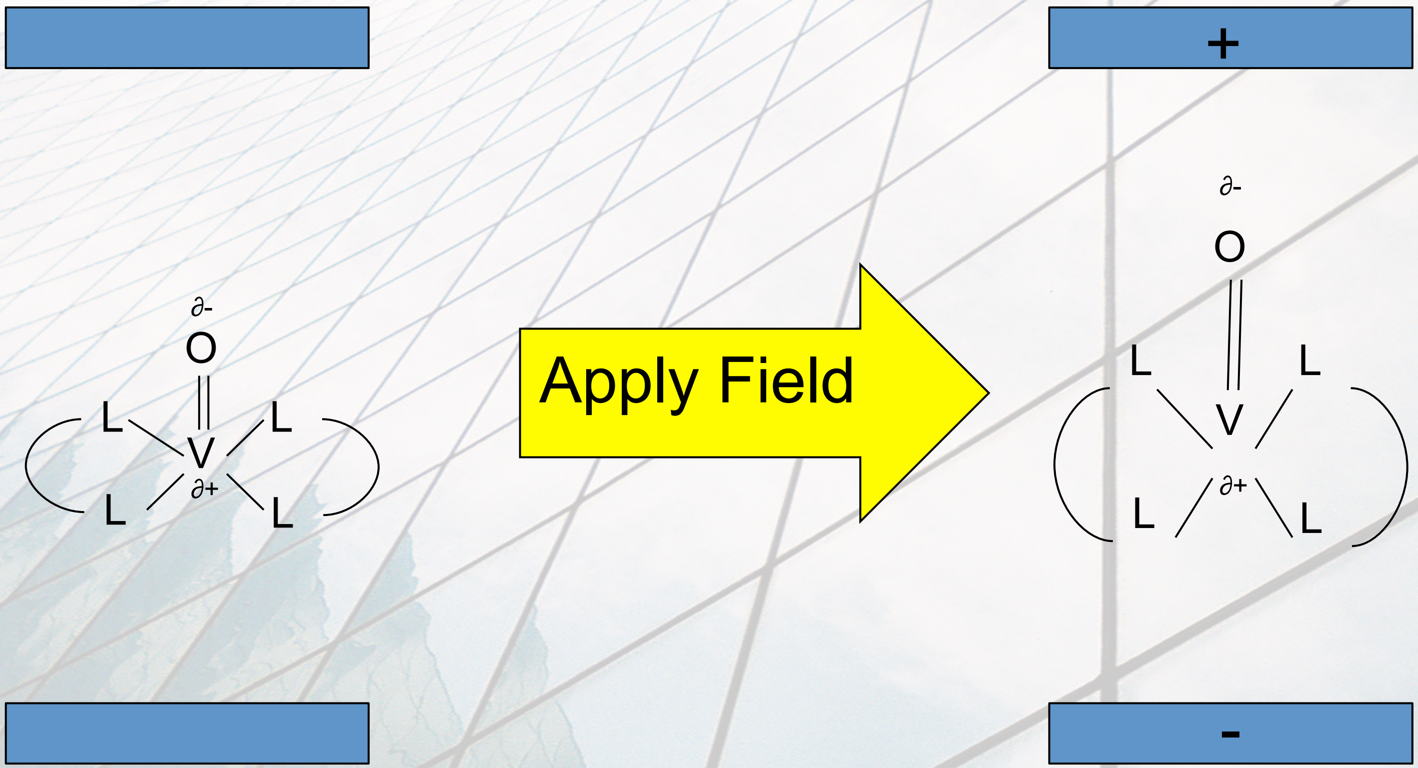


Bond Activation



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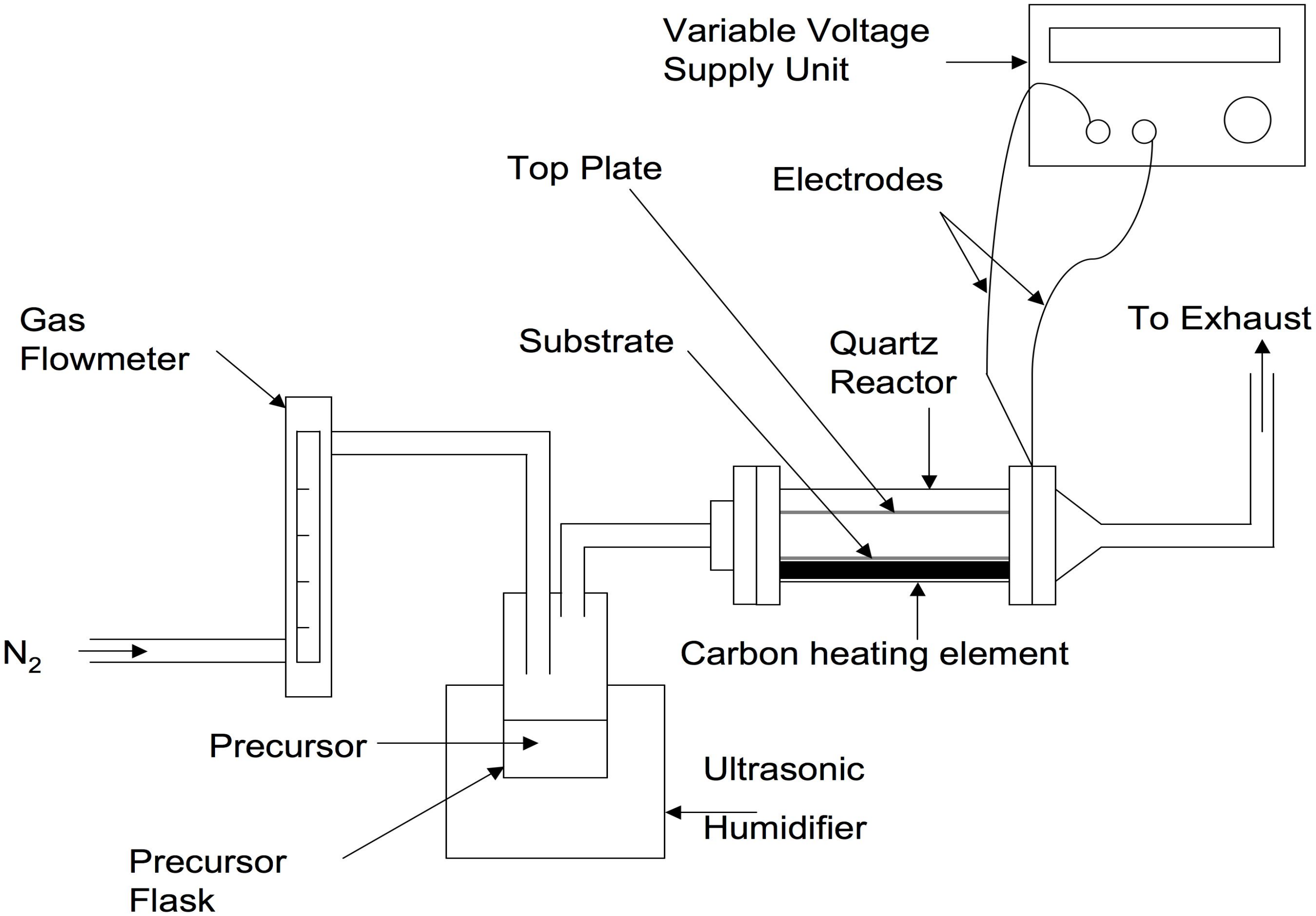

Reactor: Quartz Cold Wall

Precursor: 15 mls of 0.1 M solution of $[VO(acac)_2]$ in ethanol

Carrier Gas: N_2 at flow of 1.5 $L.min^{-1}$

Substrate Temperature: 525 ºC

Deposition Time: 1, 2, 5, 10, 20 or 30 minutes

Electric Field Strength: $1 \times 10^2 - 3 \times 10^4$ Vm^{-1} (1-30 Volts)

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Electric Field Assisted CVD

Results

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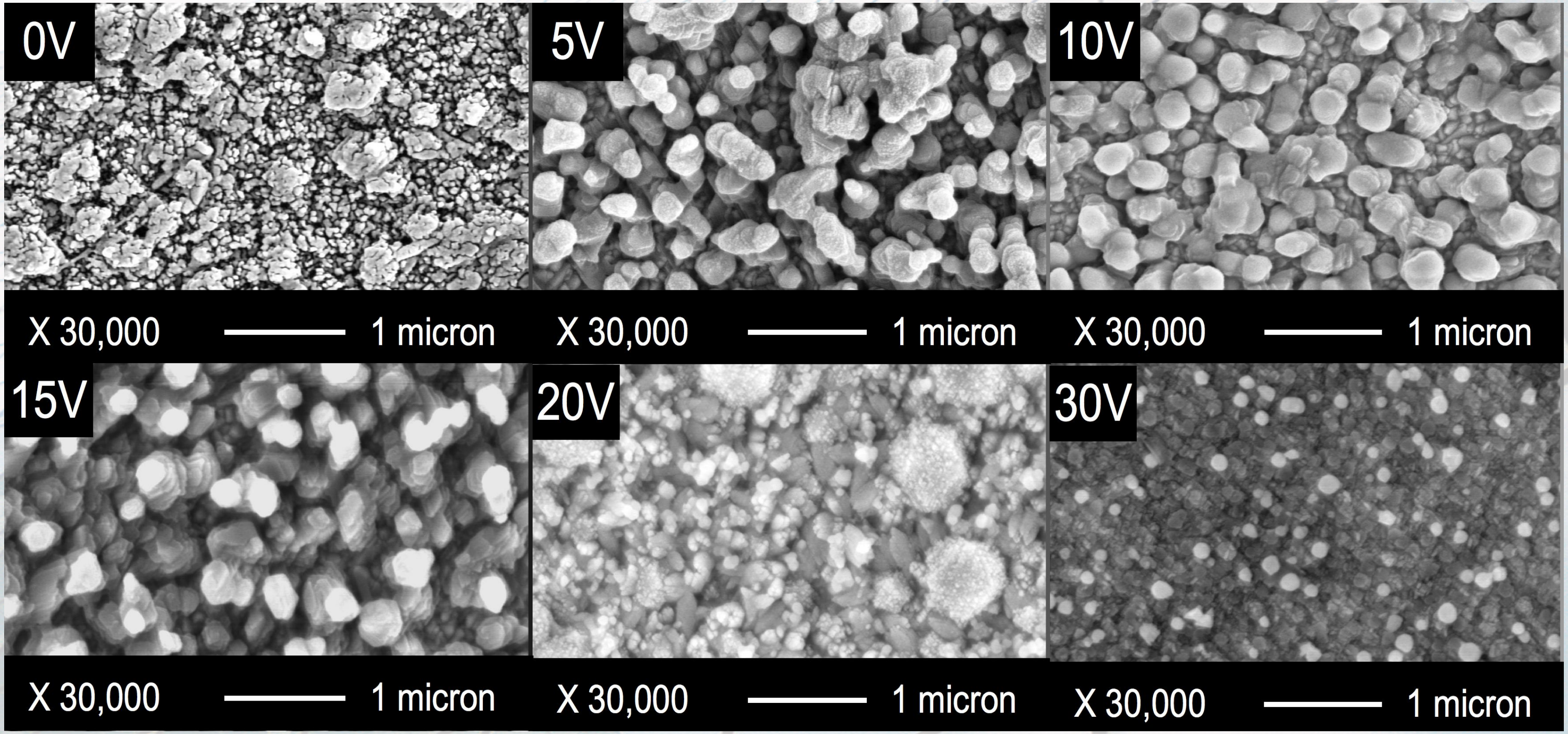
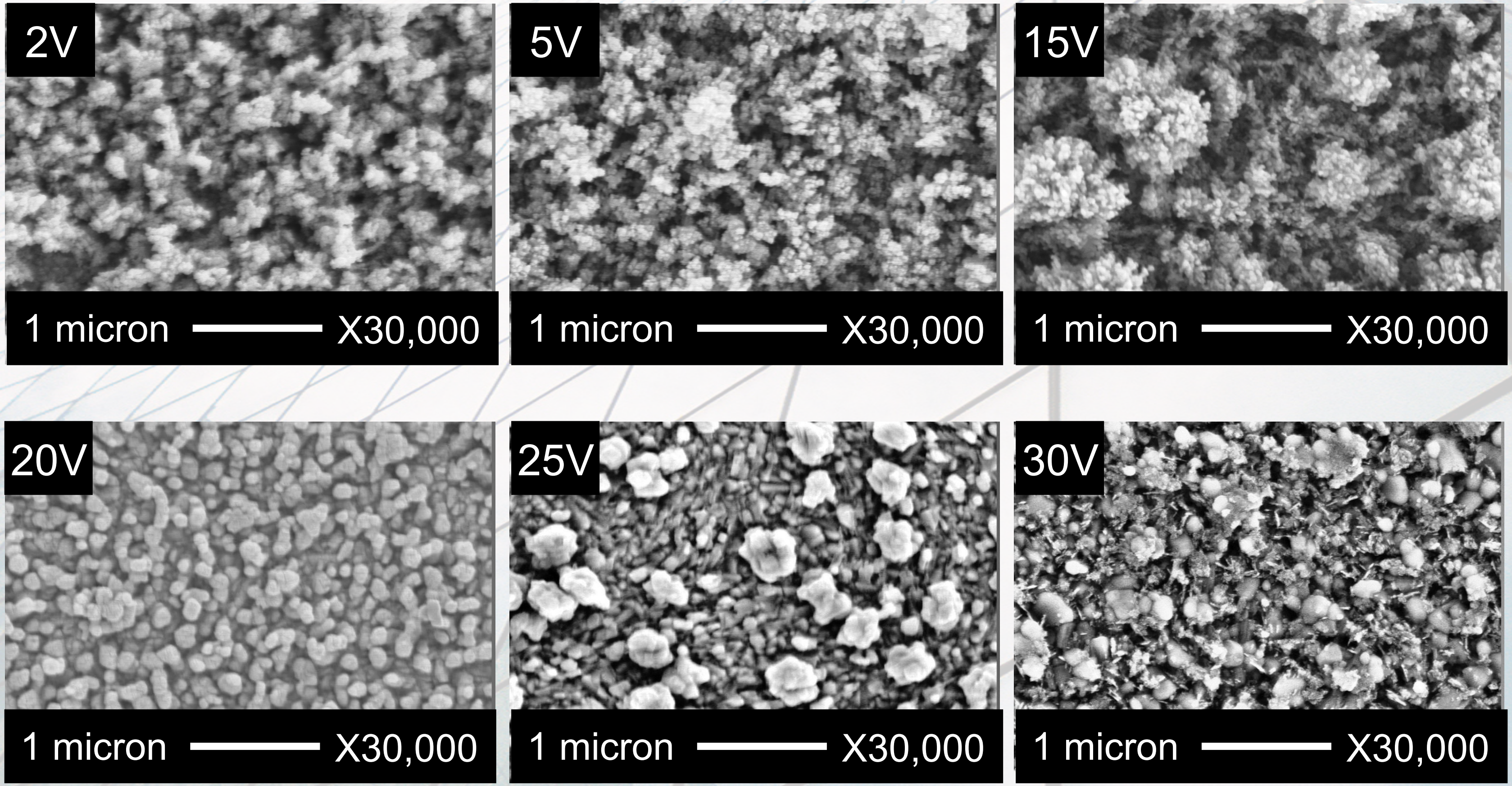
AC Field



DC Field, +ve Substrate Bias



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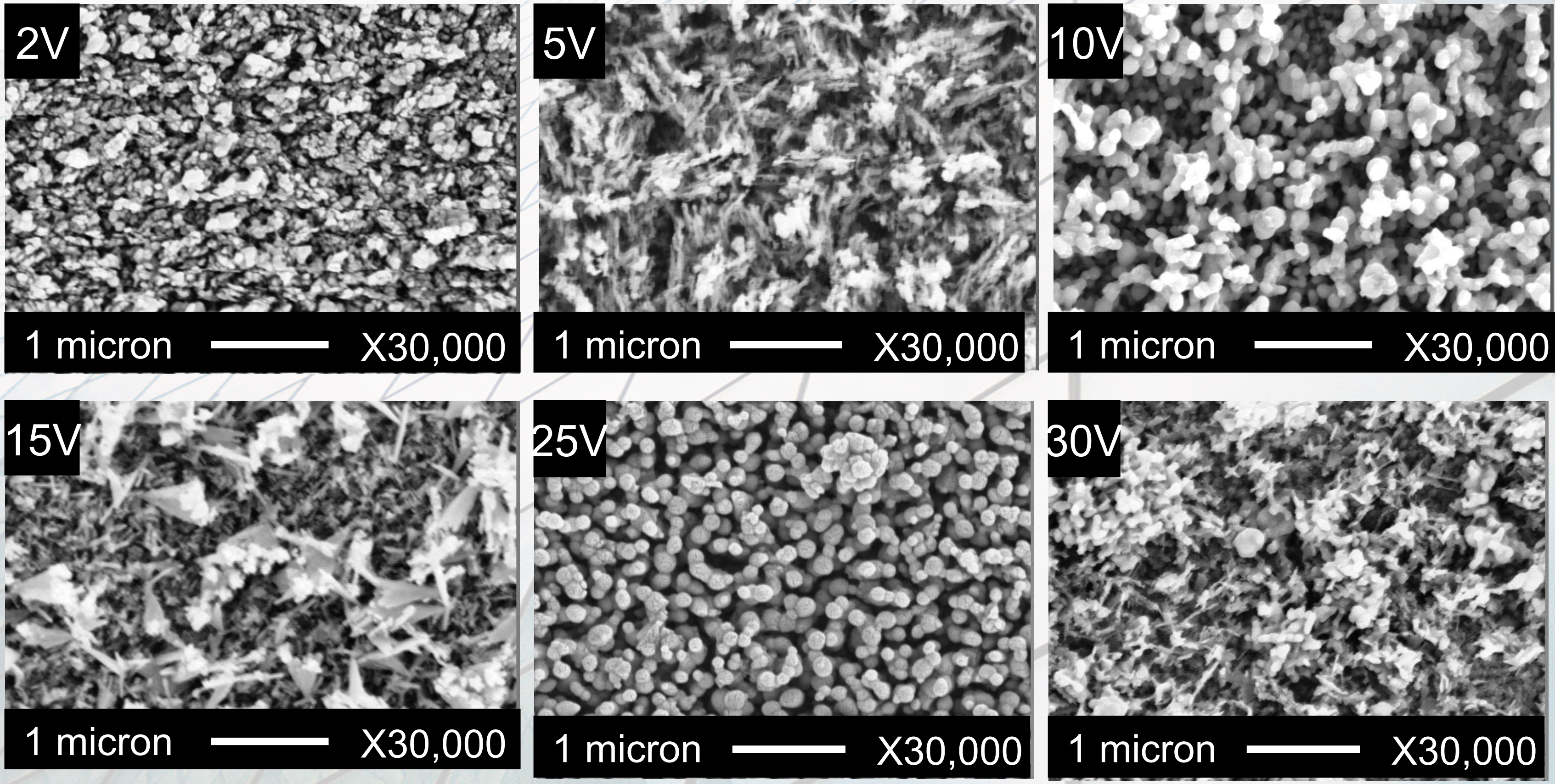
DC Field, -ve Substrate Bias



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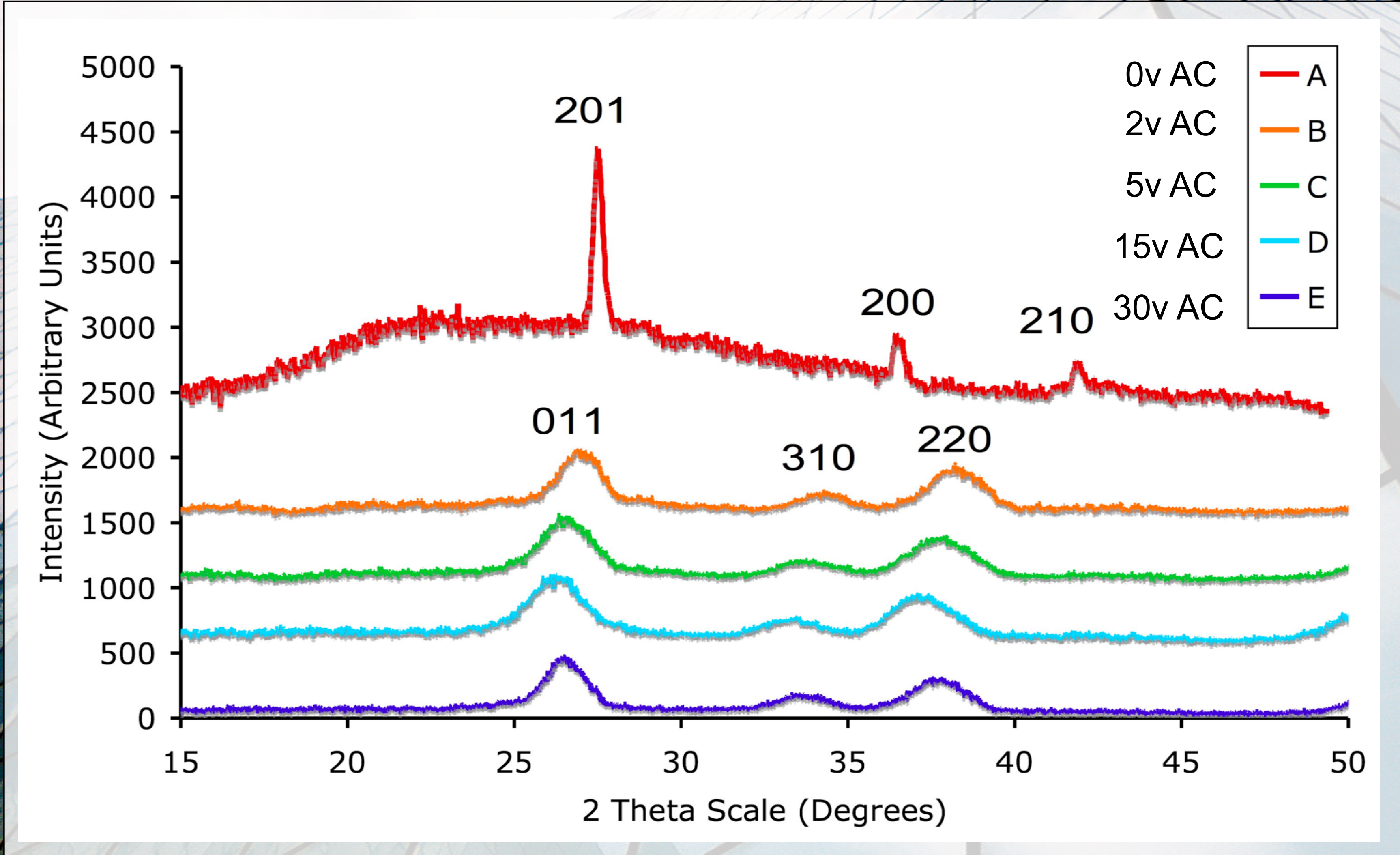

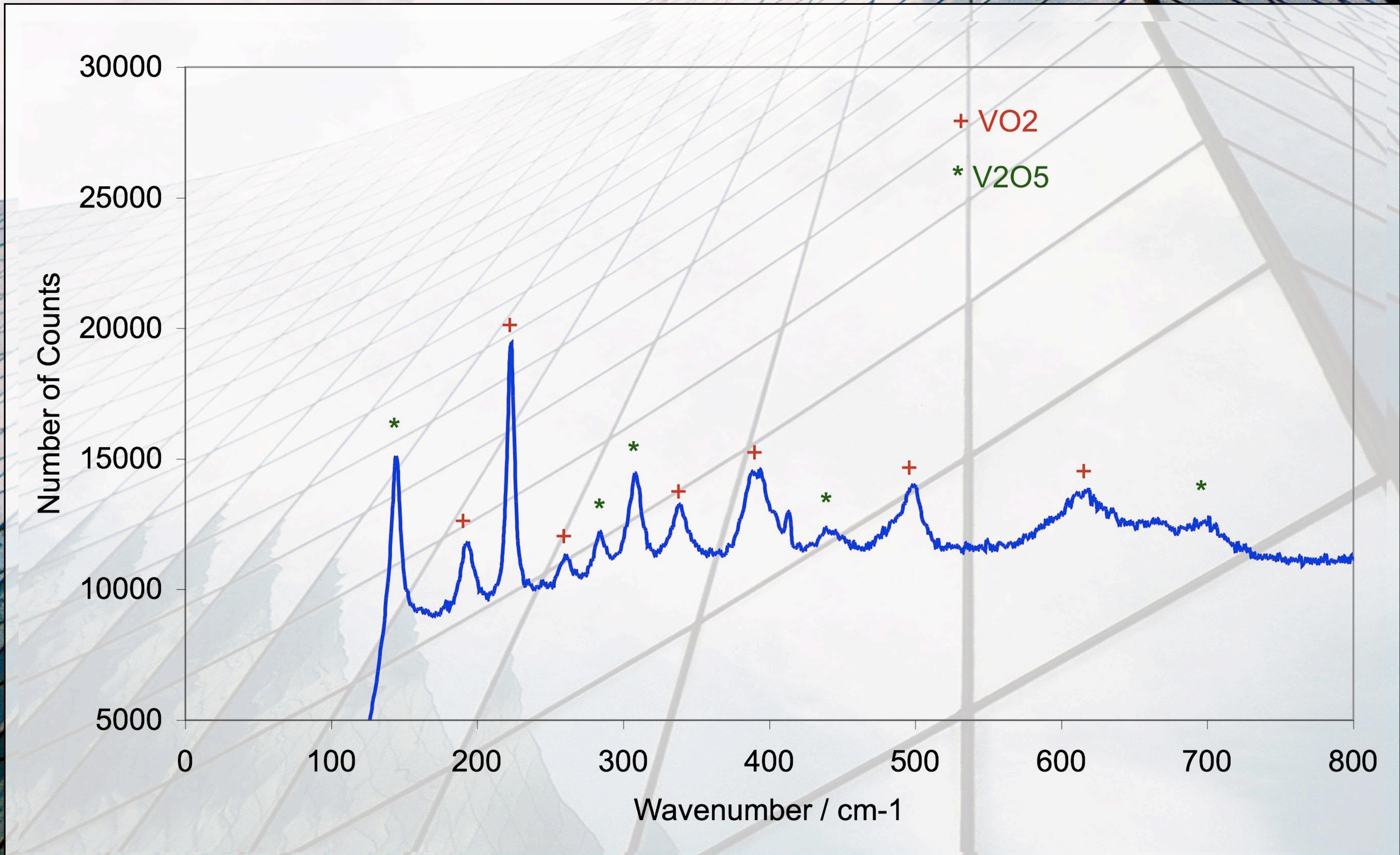
+ VO2
* V2O5
Number of Counts
30000
25000
20000
15000
10000
5000
0
100
200
300
400
500
600
700
800
Wavenumber / cm-1

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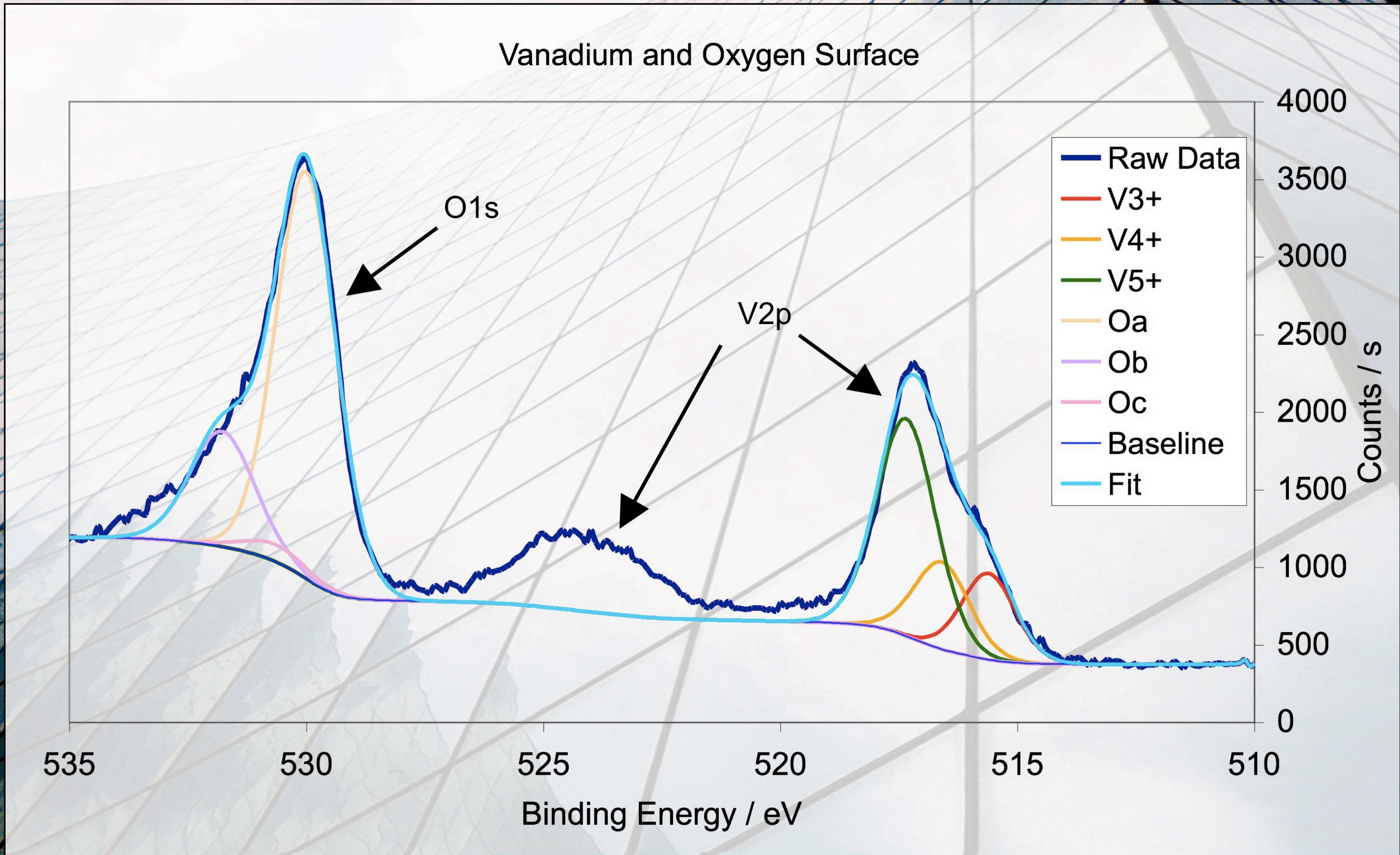

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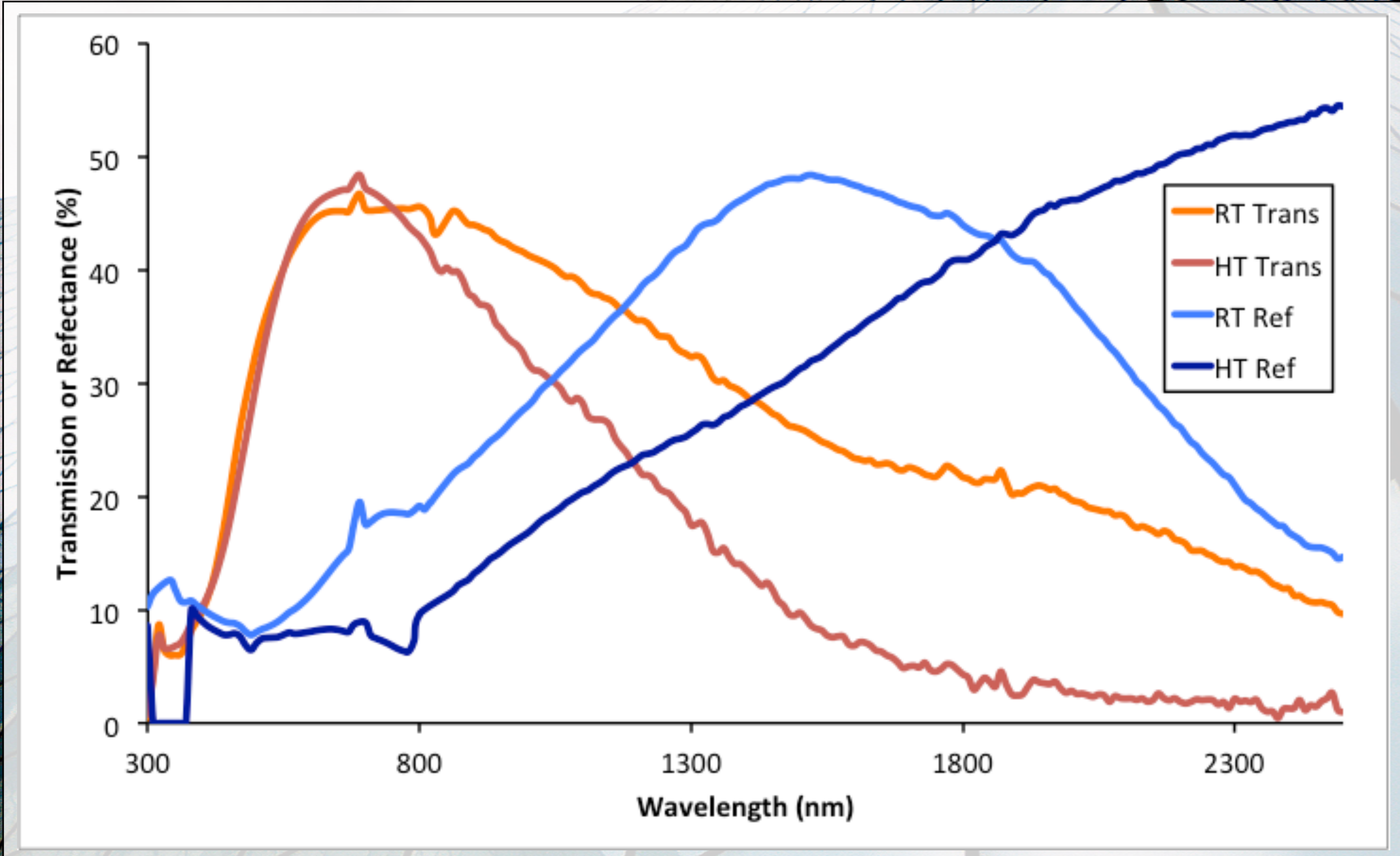

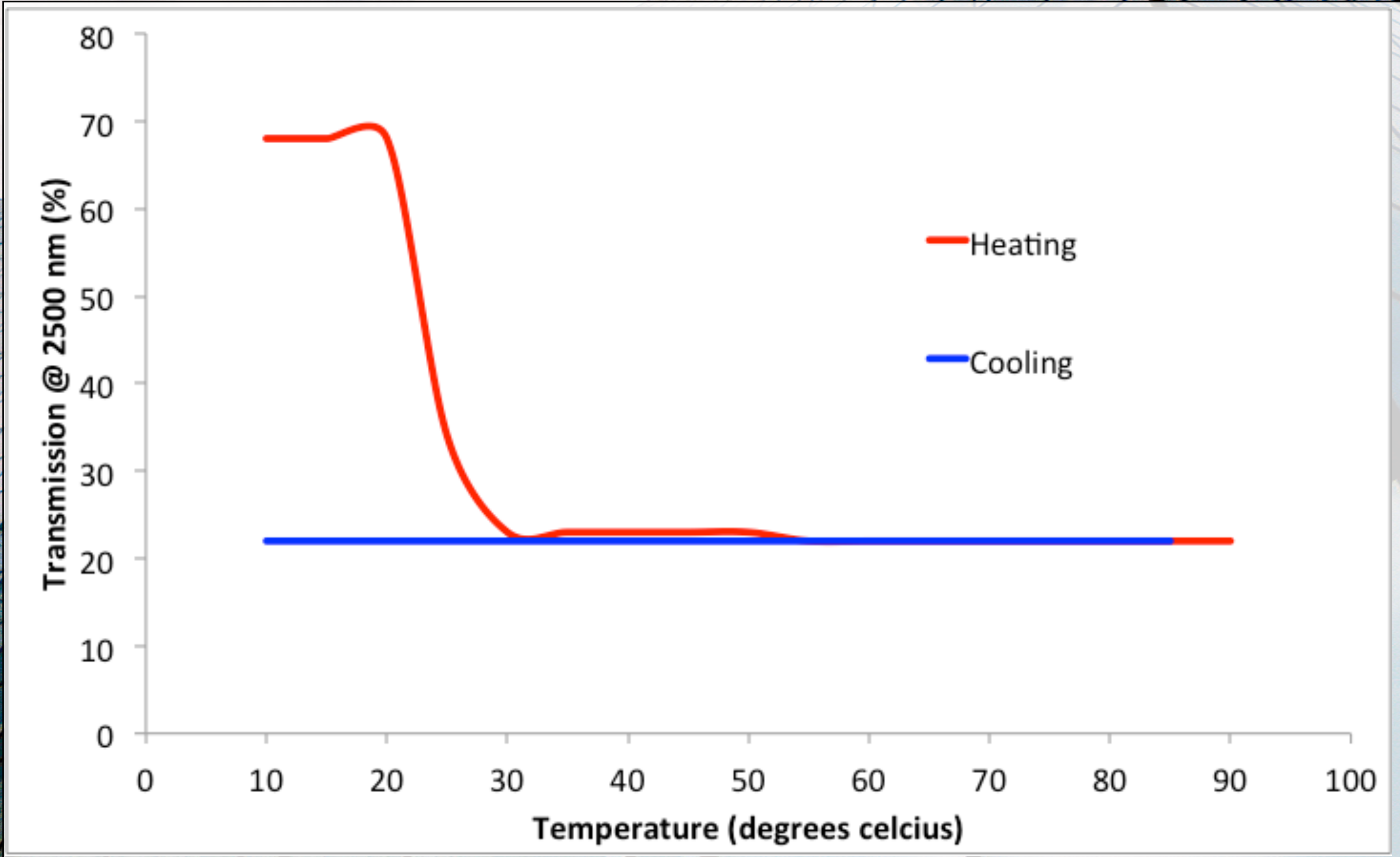
Transmission @ 2500 nm (%)
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
70
80
90
100
Temperature (degrees celcius)
Heating
Cooling

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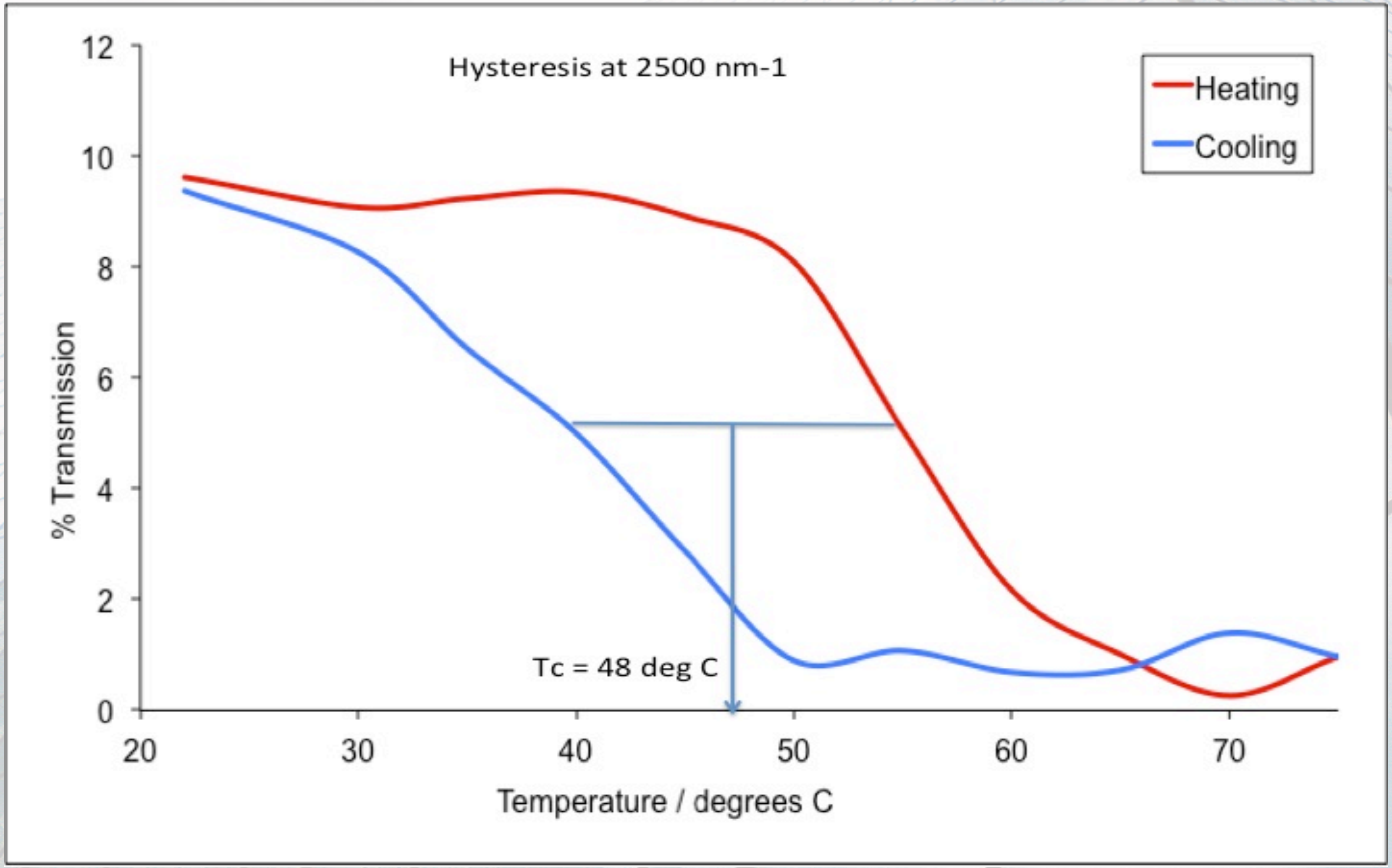
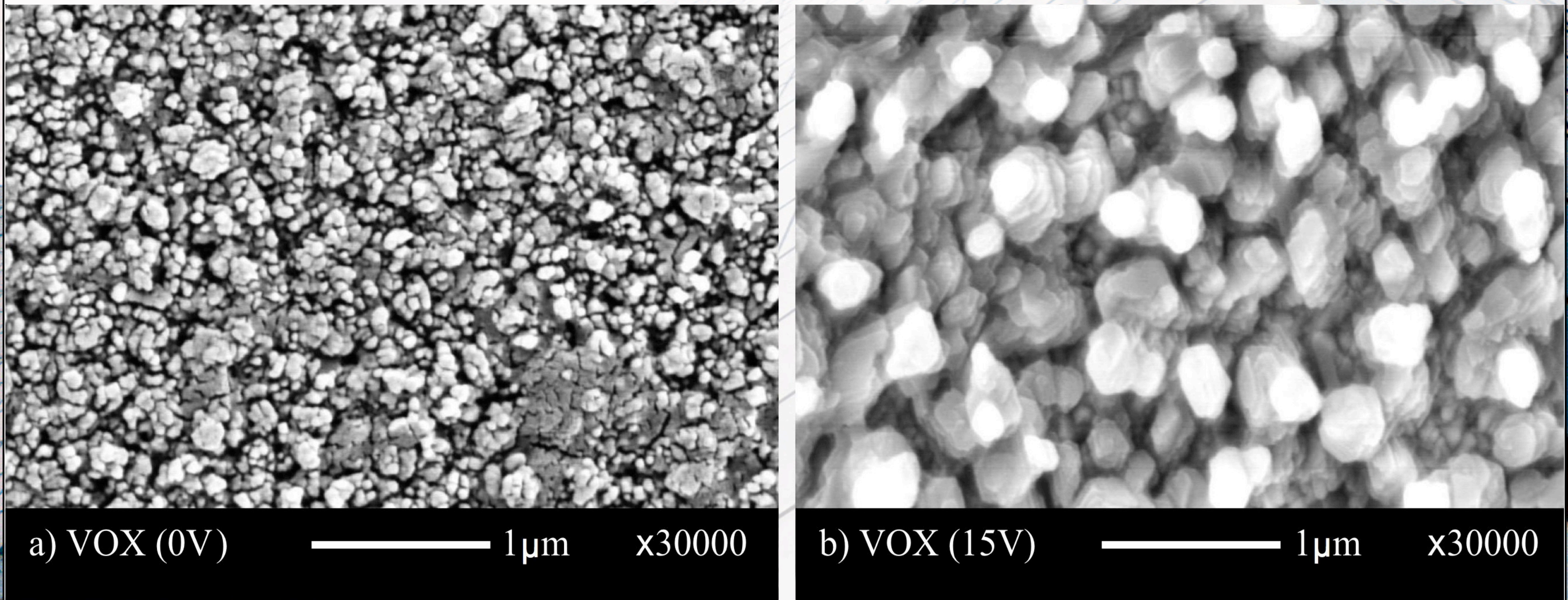
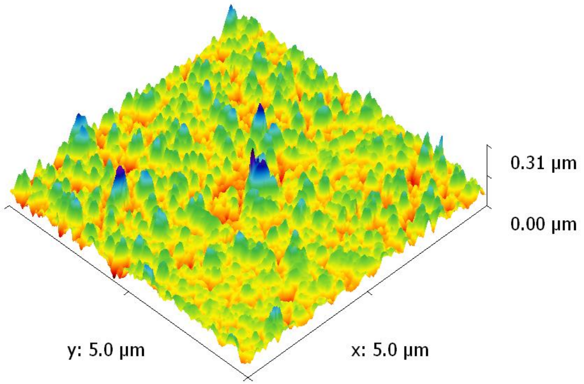


How did we do?



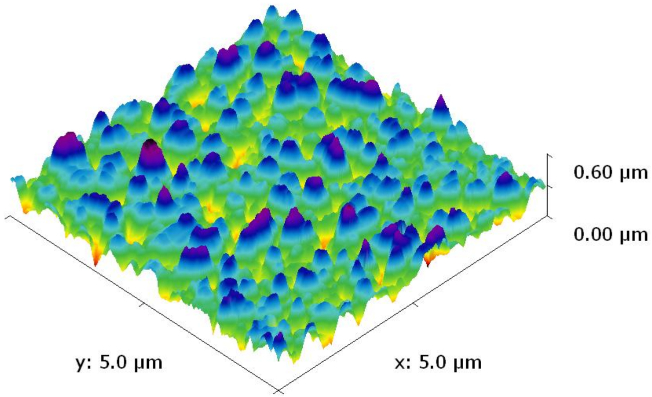
Under certain conditions, structured growth

0 V



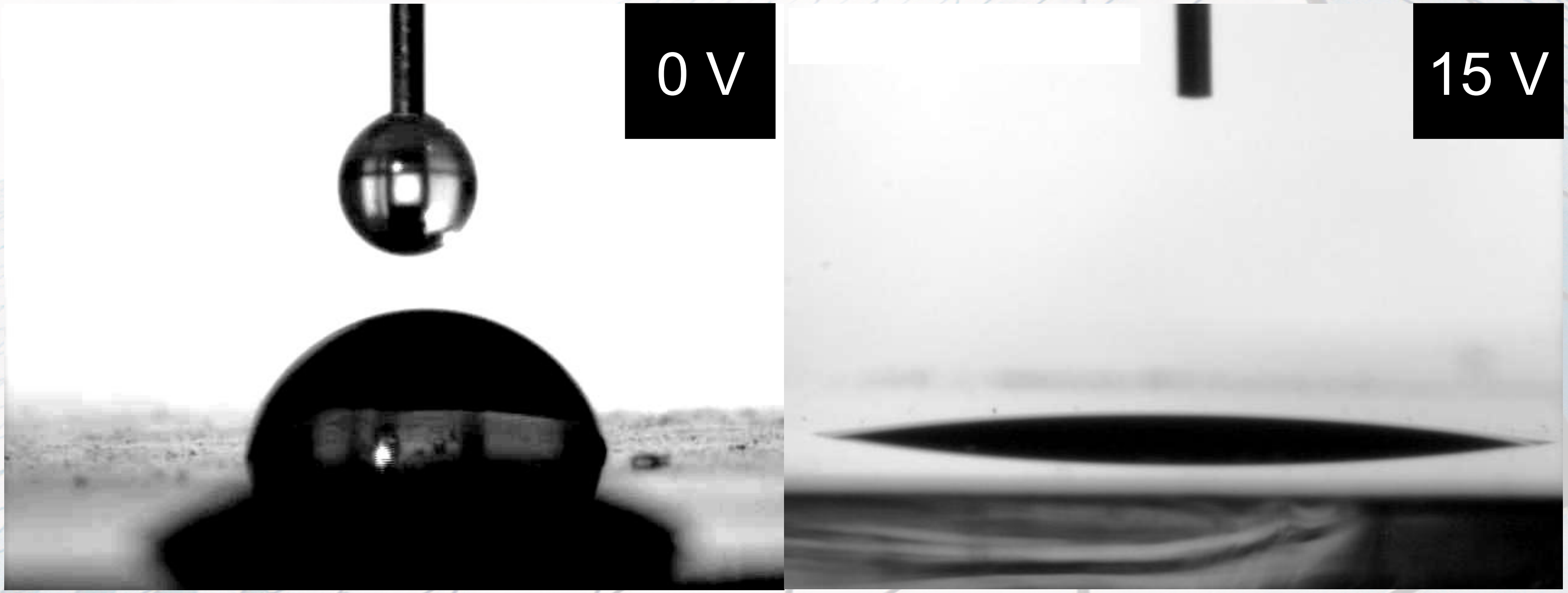
Roughness = 27.4 nm

15 V AC

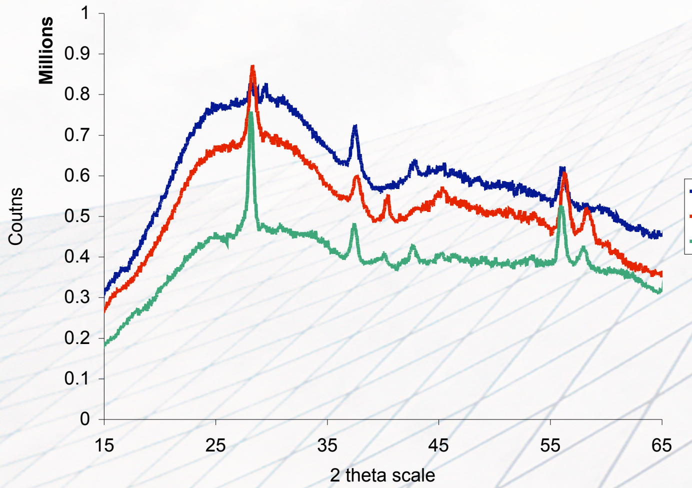


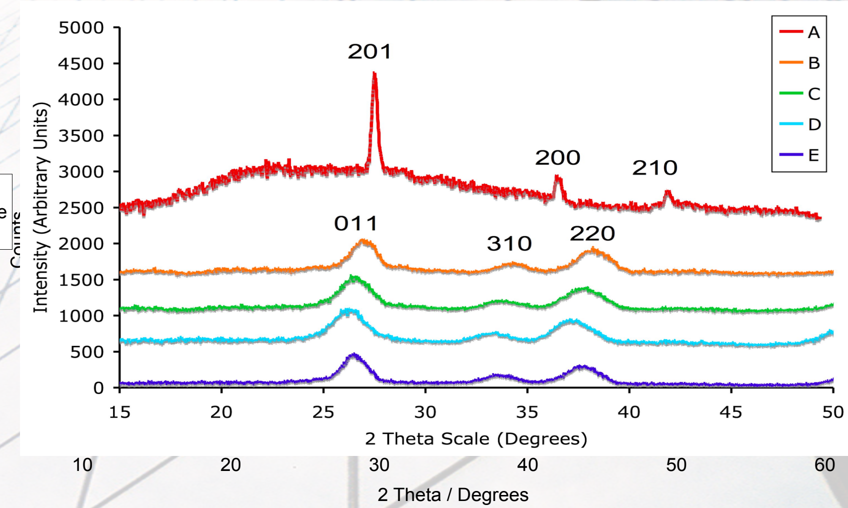
Roughness = 84.4 nm

Increased film roughness



Non UV induced super hydrophilicity





Significant peak broadening due to smaller crystallite size

Can change preferential orientation

Change in crystal cell size

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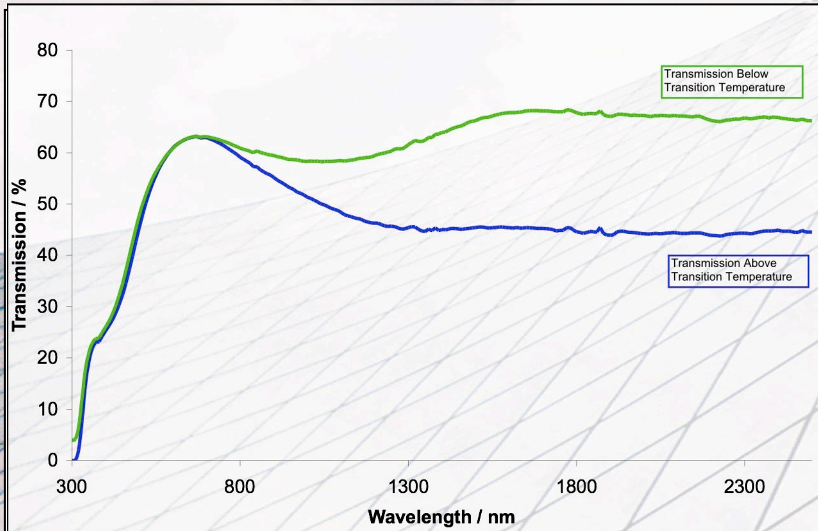

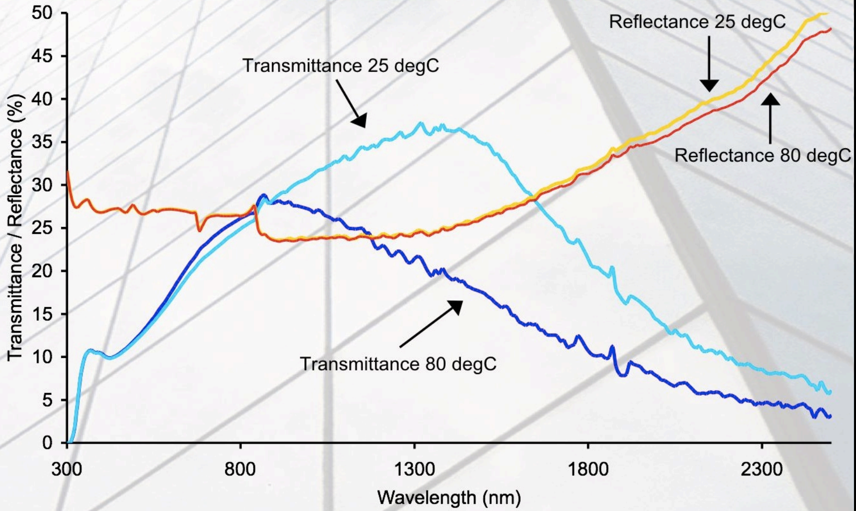

Thermochromic transition still observed, similar magnitude

Except samples with smallest crystallite sizes
(thermal oxidation at low temperatures)

Shift in optical transition onset (800 nm rather than 750 nm)

What did we learn?

Ideal thermochromic film has an instant and sharp transition occurring at a low transition temperature.

There is some room for “imperfection” before energy benefit declines.

It is possible to make films with transition properties in this window.

Possible to lower transition temperature to a desirable level using EACVD.

We need to protect our nanostructured films to avoid oxidation and preserve thermochromicity.

Thanks and Acknowledgements to:

Dr. Michael Warwick (Padova)

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Prof. Ivan Parkin (UCL)
Dr Clara Piccirillo (UCP)

Dr Ian Ridley (RMIT)
Dr Arch. Eng. Manfredi Saeli (UP)

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A variety of "ideal" spectra based on the state of the art

Maximum visible transmission set at 65 %

Transition covers the 800 - 1200 nm region

Transition temperature and transition magnitude varied

Hysteresis effects not modelled in initial work

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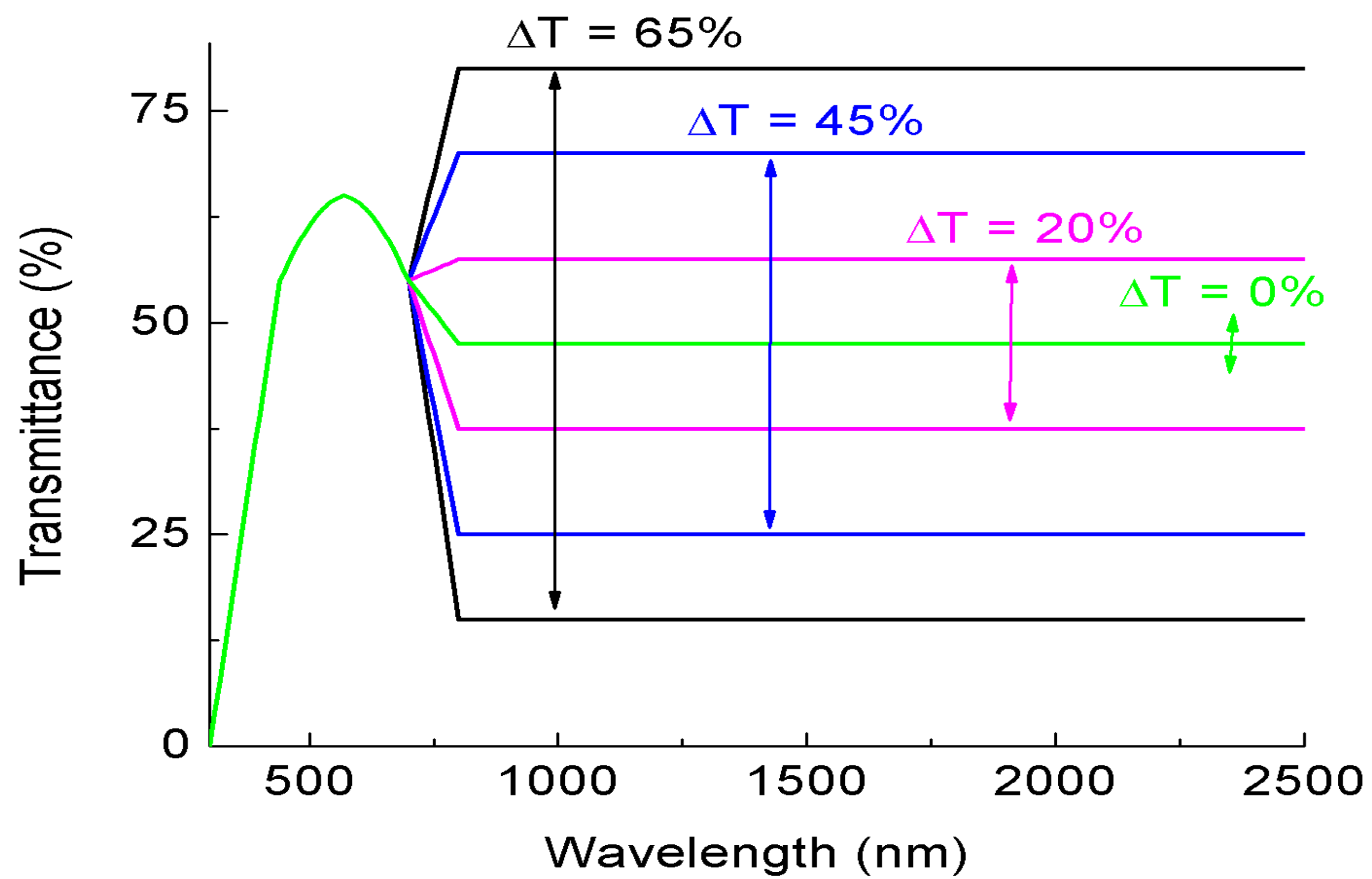

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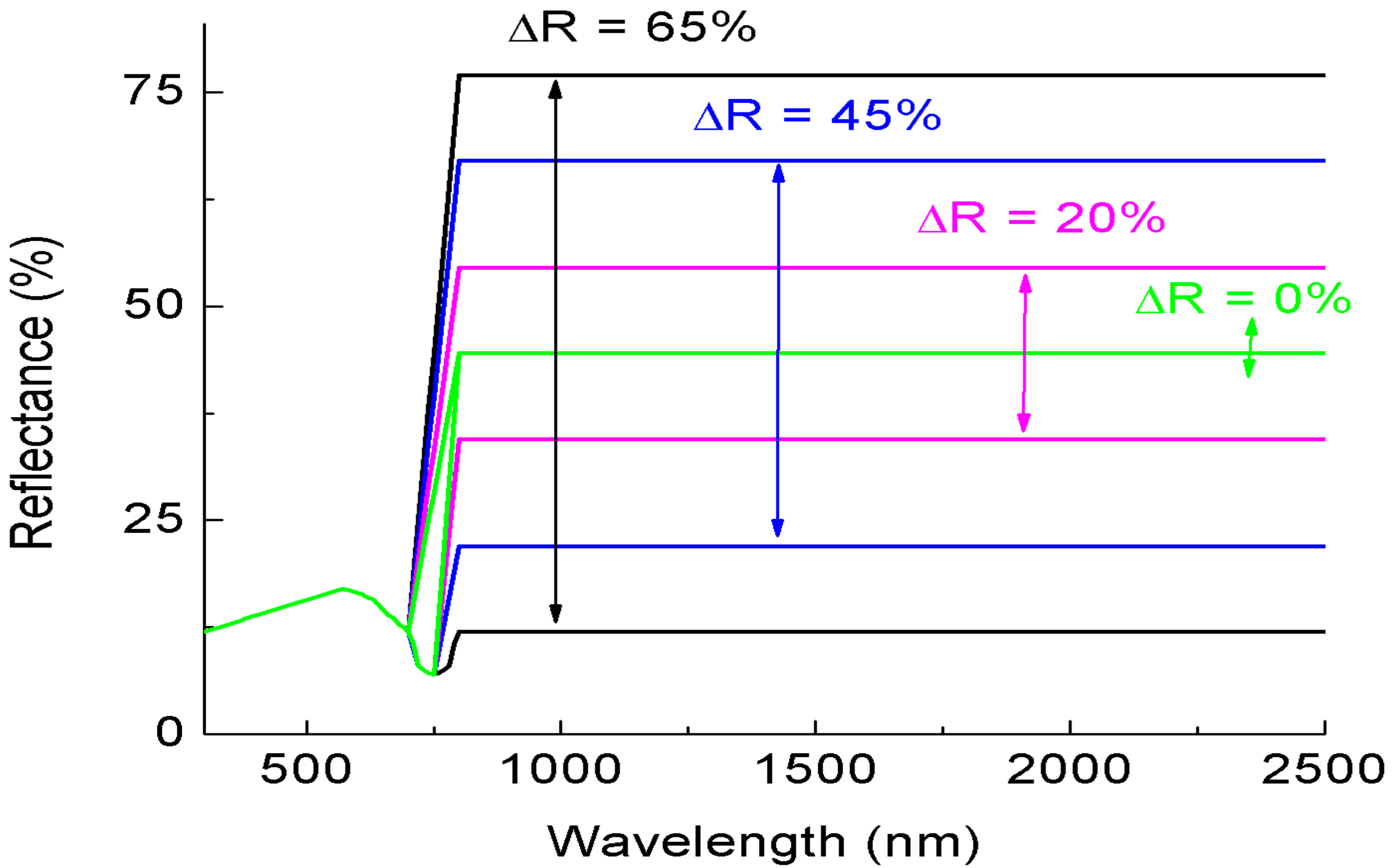

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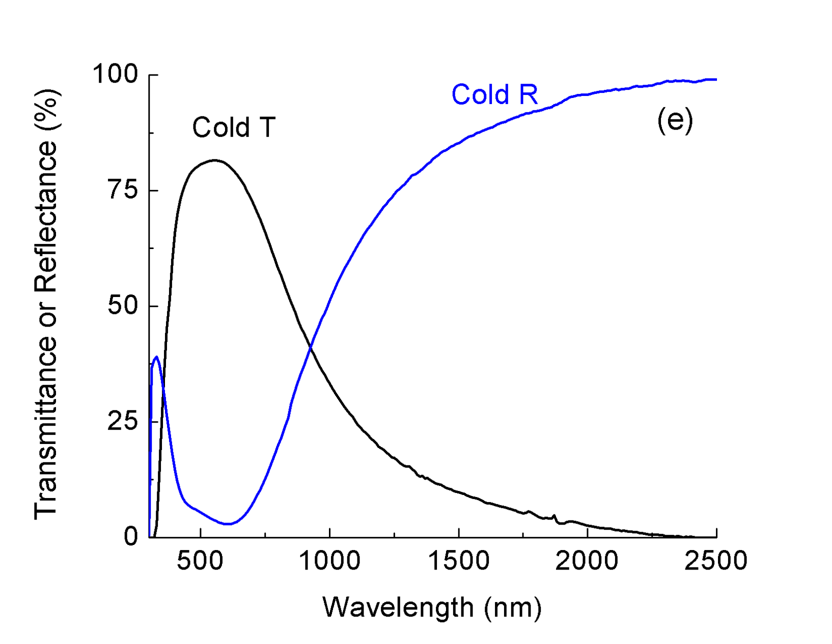

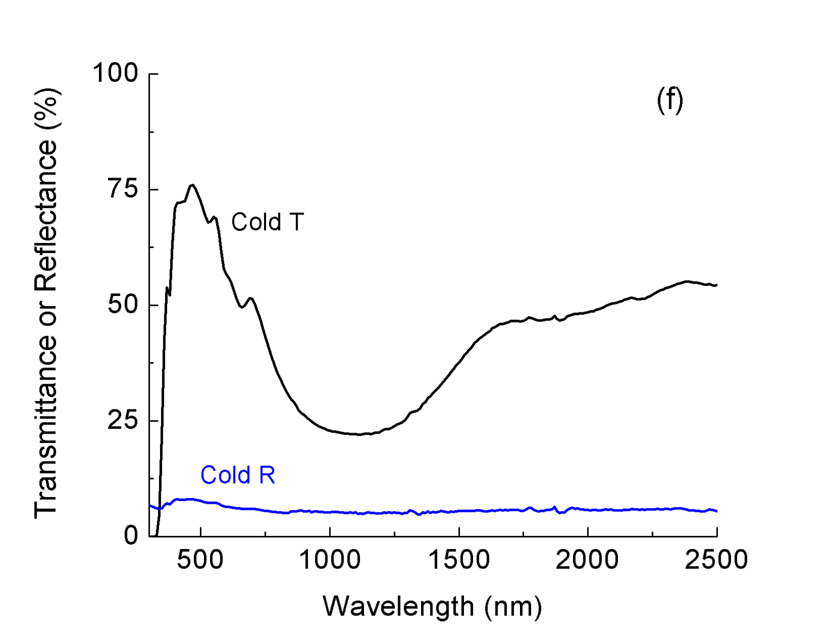

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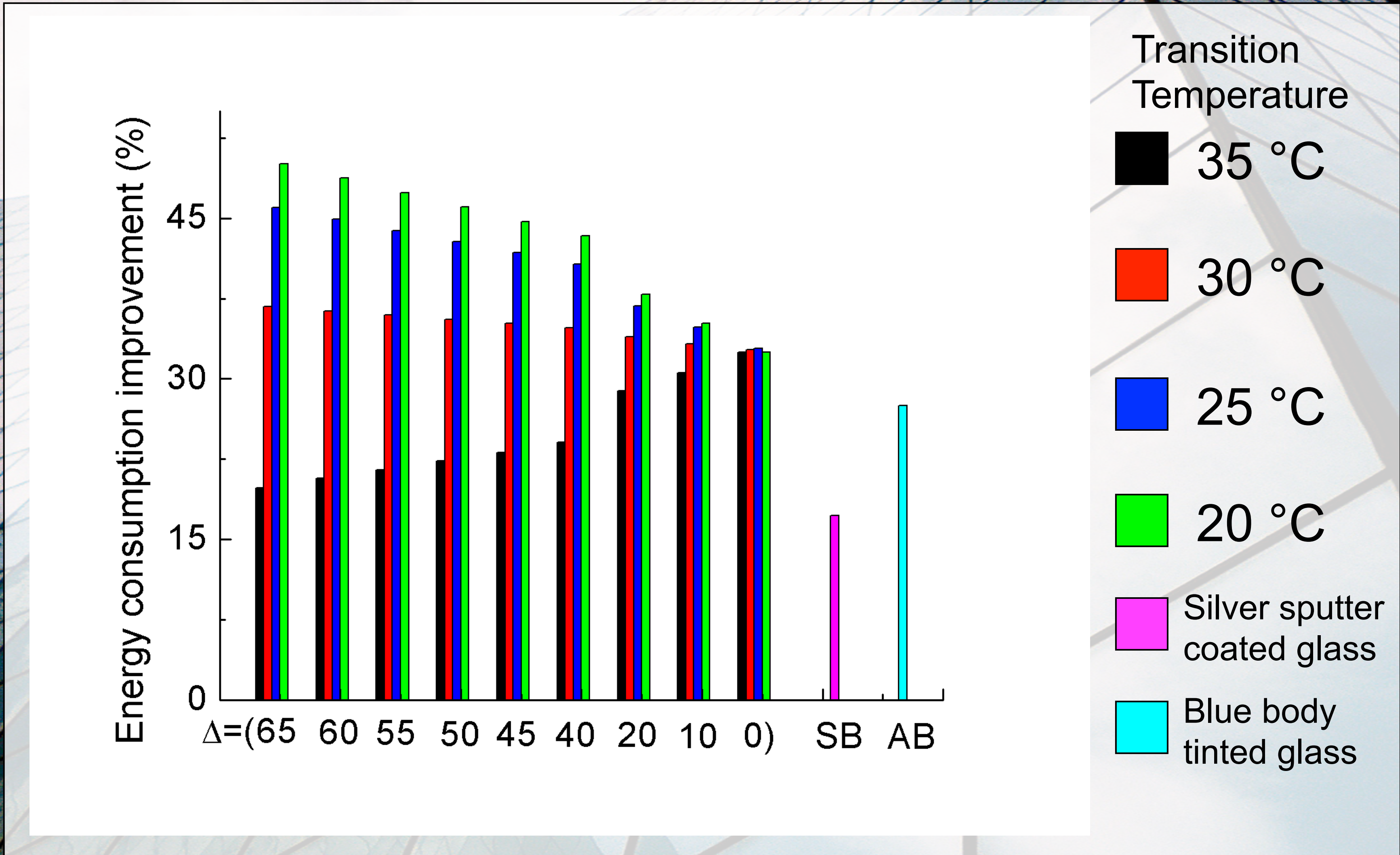

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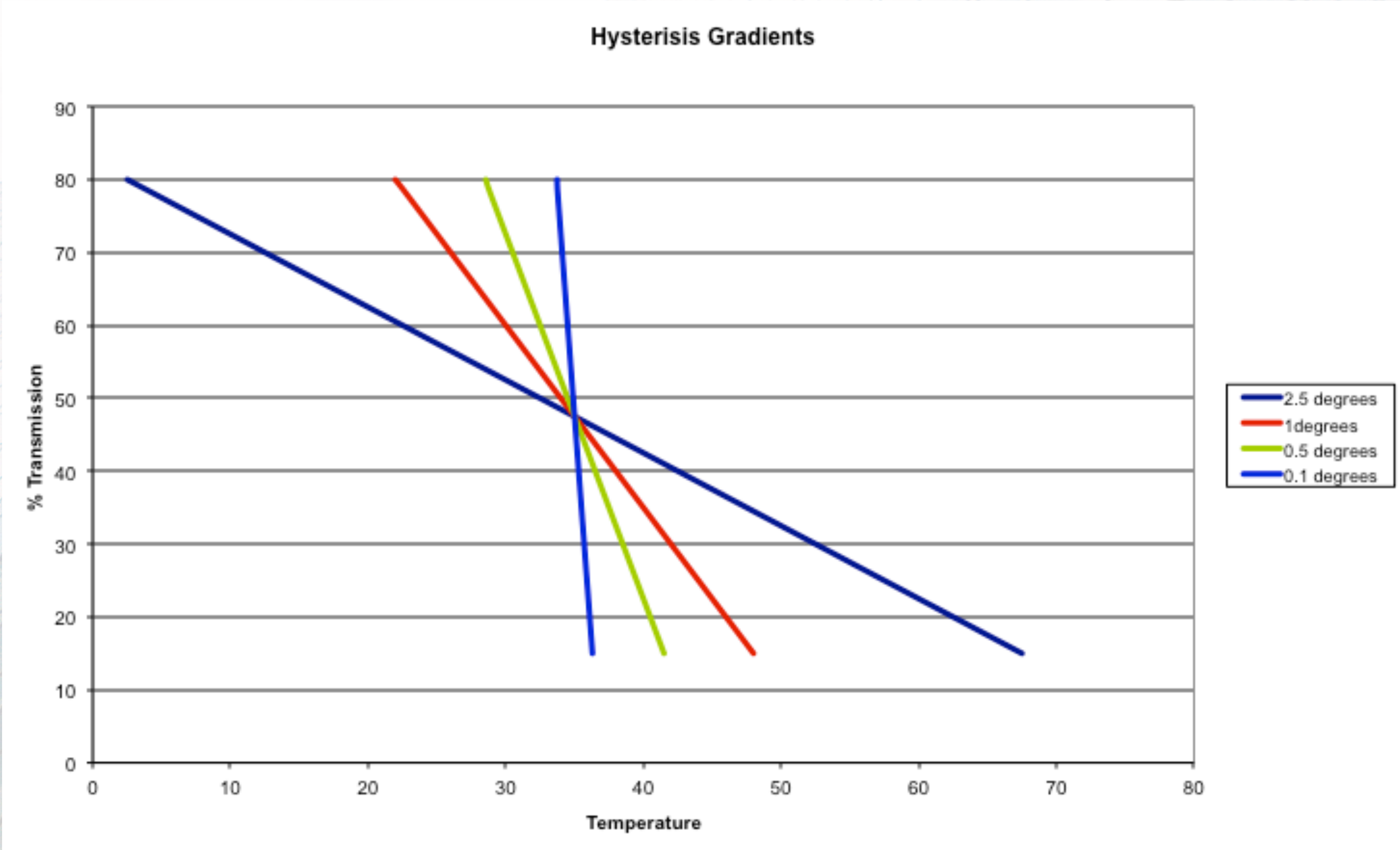

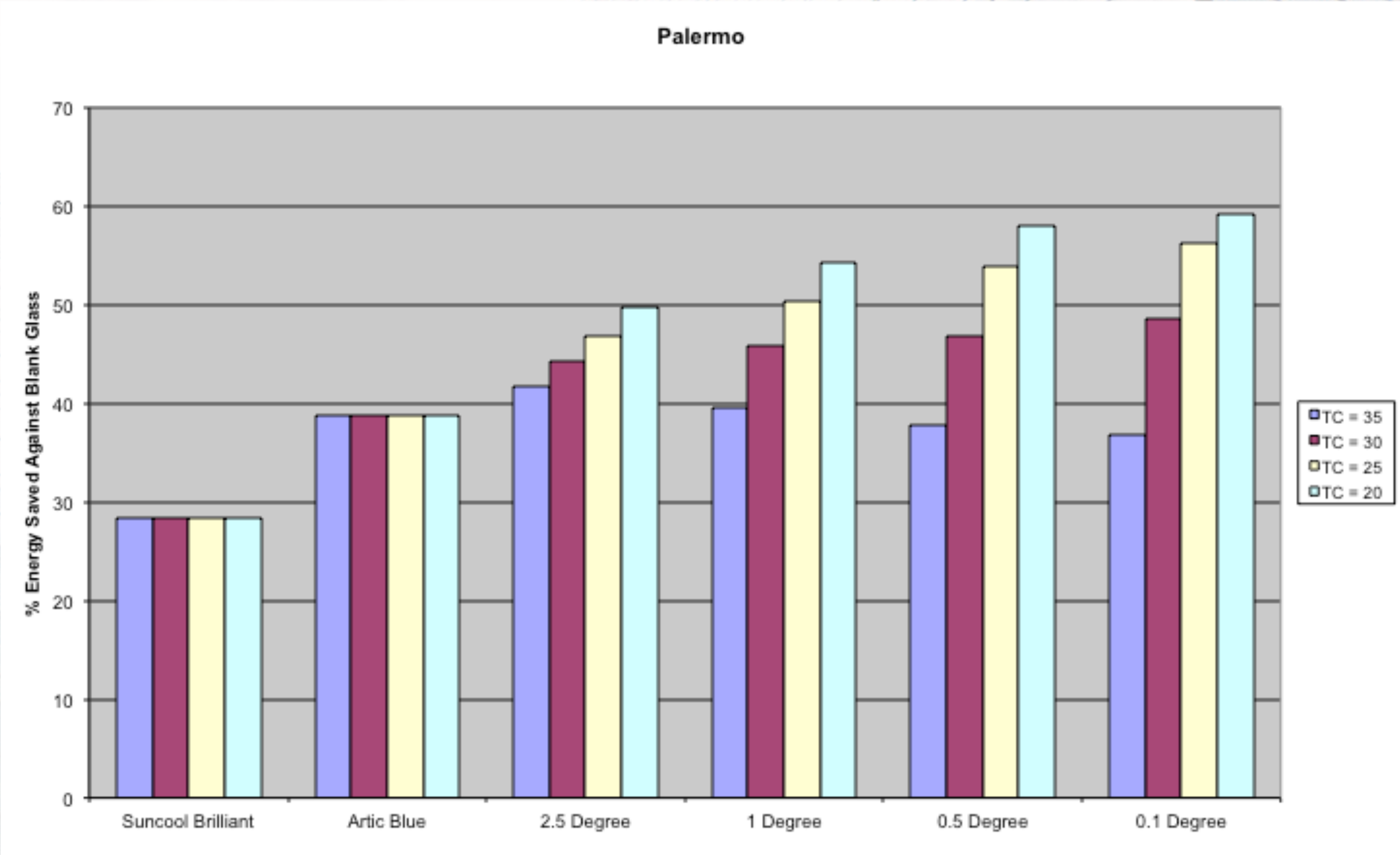
Palermo
% Energy Saved Against Blank Glass
70
60
50
40
30
20
10
0
Suncool Brilliant
Artic Blue
2.5 Degree
1 Degree
0.5 Degree
0.1 Degree
TC = 35
TC = 30
TC = 25
TC = 20

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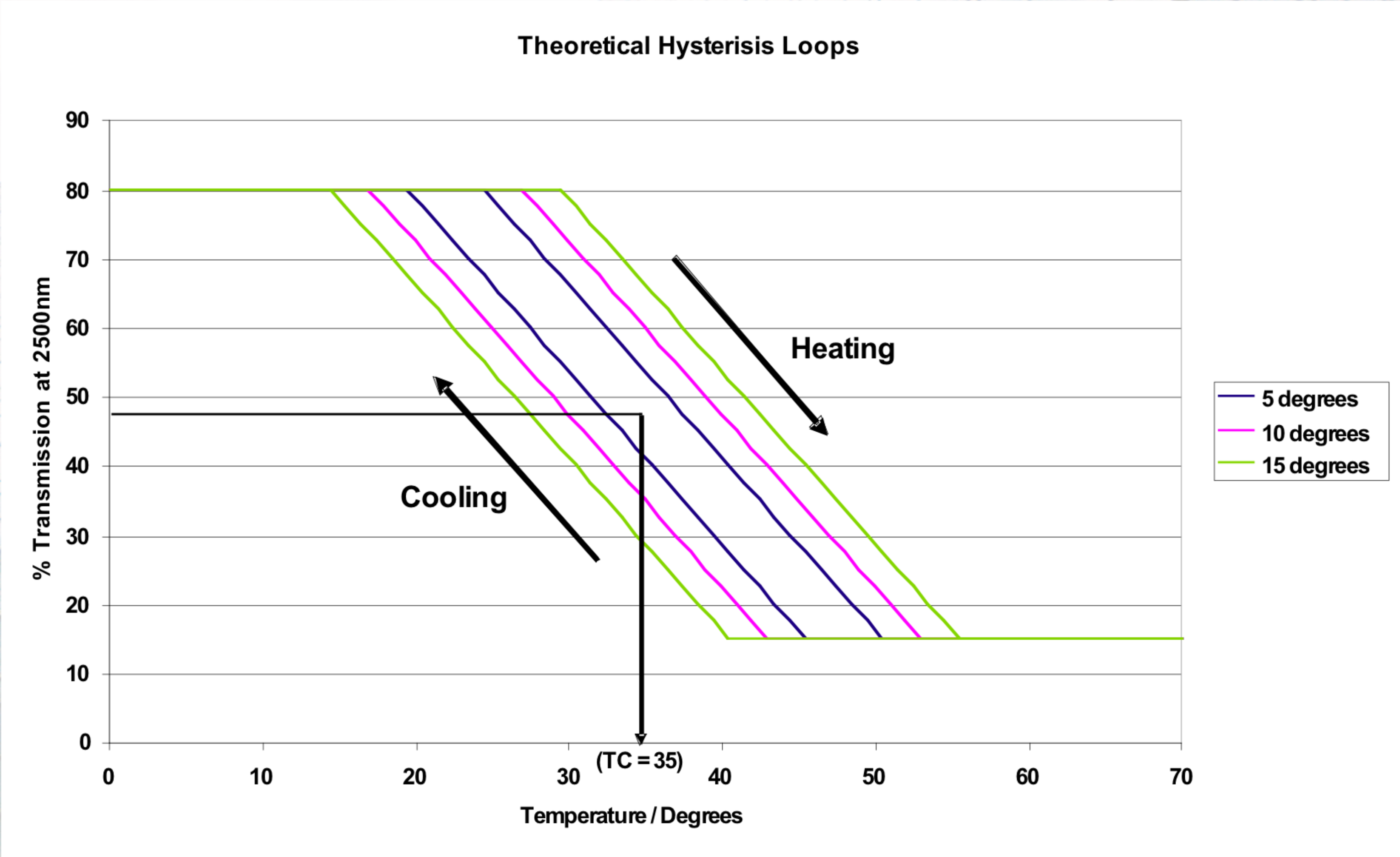

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