Design of high-performance VO_2-based thermochromic coatings, and pathway for their industry-friendly preparation

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DEPARTMENT OF PHYSICS

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Acknowledgment

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Basis of outline and figures

Recent invited Perspective paper

J. Houska, *Design and reactive magnetron sputtering of thermochromic coatings*, J. Appl. Phys. 131, 110901 (2022)

- results of our lab:
  prof. J. Vlcek, J. Rezek, D. Kolenaty, T. Barta, ...
- results of other labs (reused with publishers' permission):
  profs. P. Jin, P.J. Klar, C.G. Granqvist, L. Martinu, ...

Outline

I. Introduction and background

II. Quantities of interest and criteria of success

III. Properties and sputtering of thermochromic VO_2

IV. Ways to improve the coating characteristics

    A. Suitable doping elements

    B. Suitable materials of antireflection layers

    C. Design of multilayers with optimized ΔT_{sol} and T_{lum}

    D. Design of multilayers with optimized ΔT_{sol} and color

    E. Designs based on layers containing VO_2 nanoparticles

    F. Decreasing the coating emissivity in the infrared

V. Sputtering of high-performance VO_2-based multilayers

VI. Summary and outlook

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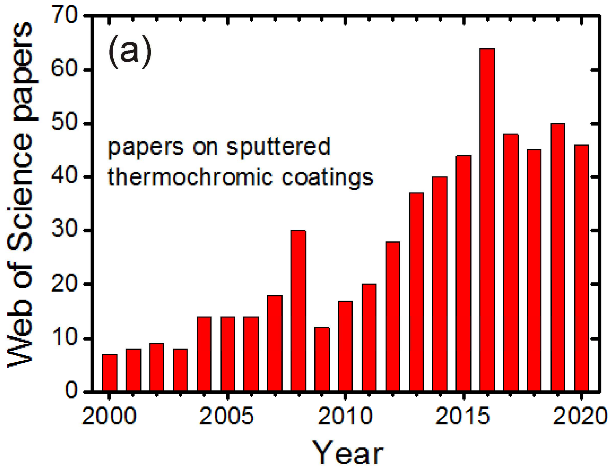
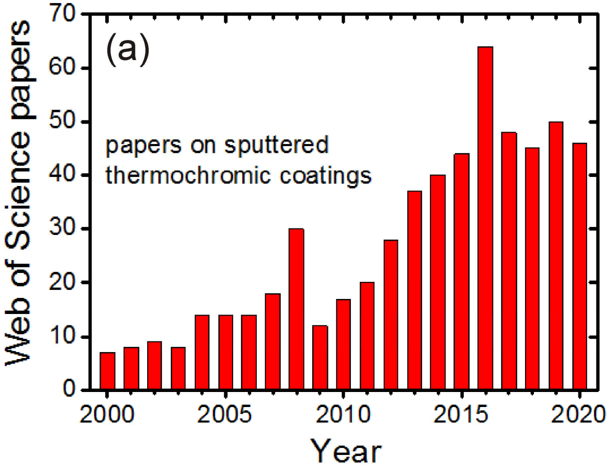
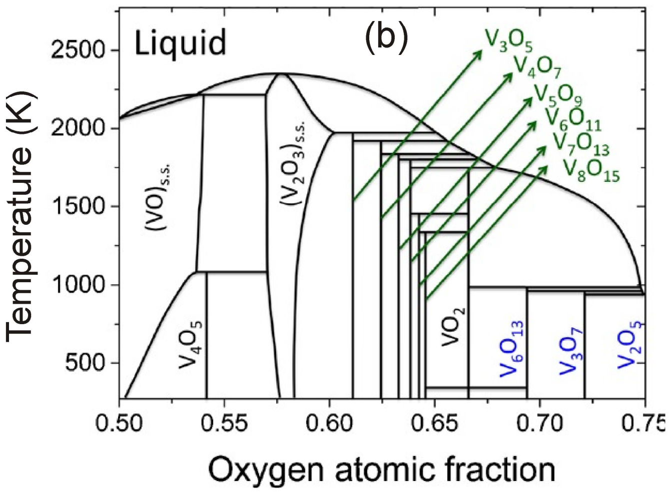


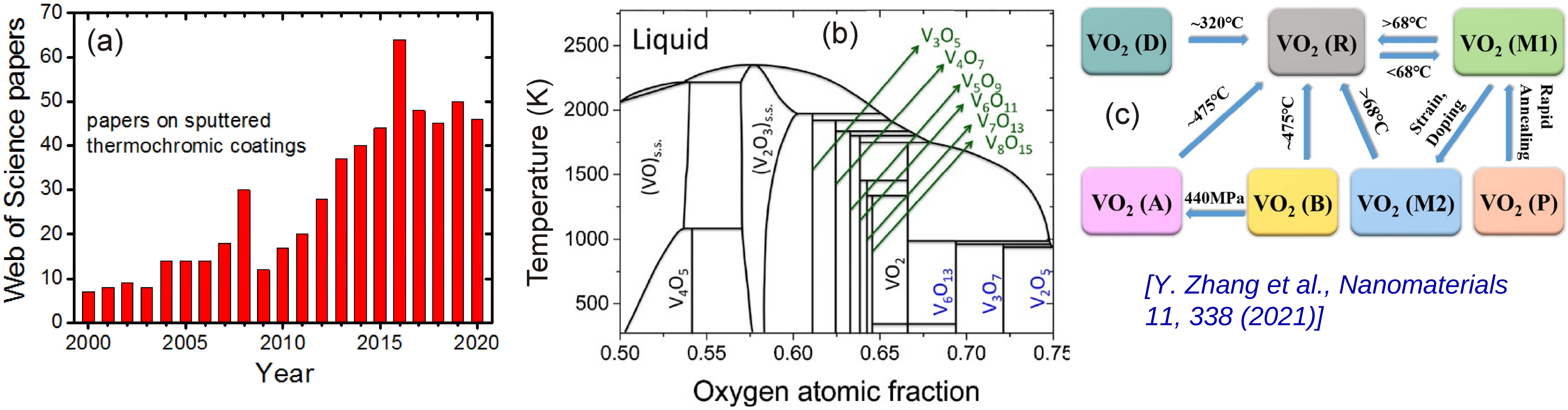
Era of interest in energy-saving applications $\Rightarrow$
enhanced number of papers on thermochromic coatings,
predominantly based on $VO_2(M1) \underset{\approx 68°C}{\Leftrightarrow} VO_2(R)$





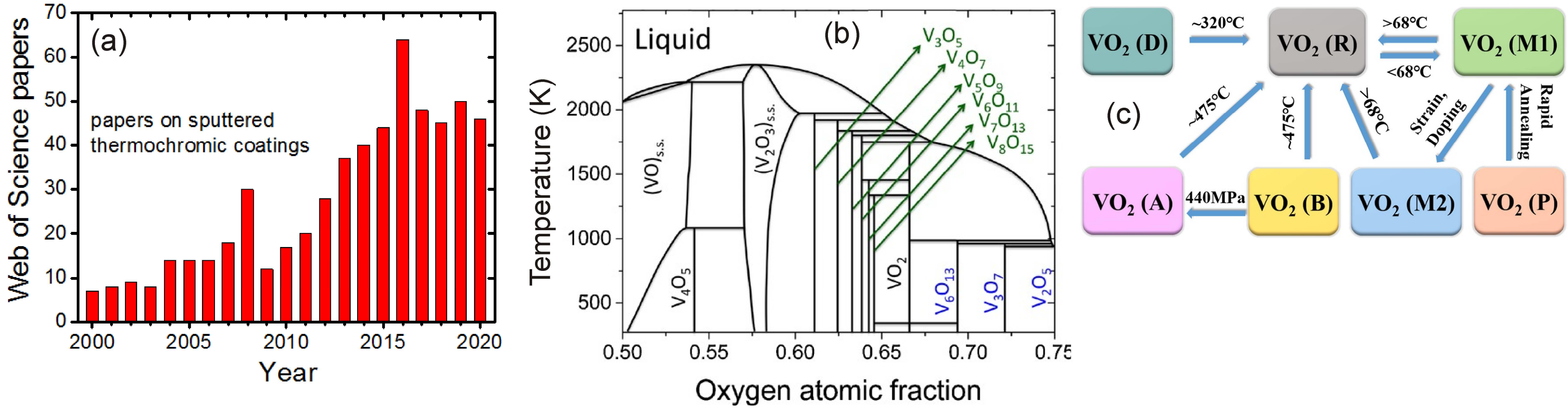
[Y.B. Kang, J. Eur. Ceram. Soc. 32, 3187 (2012)]

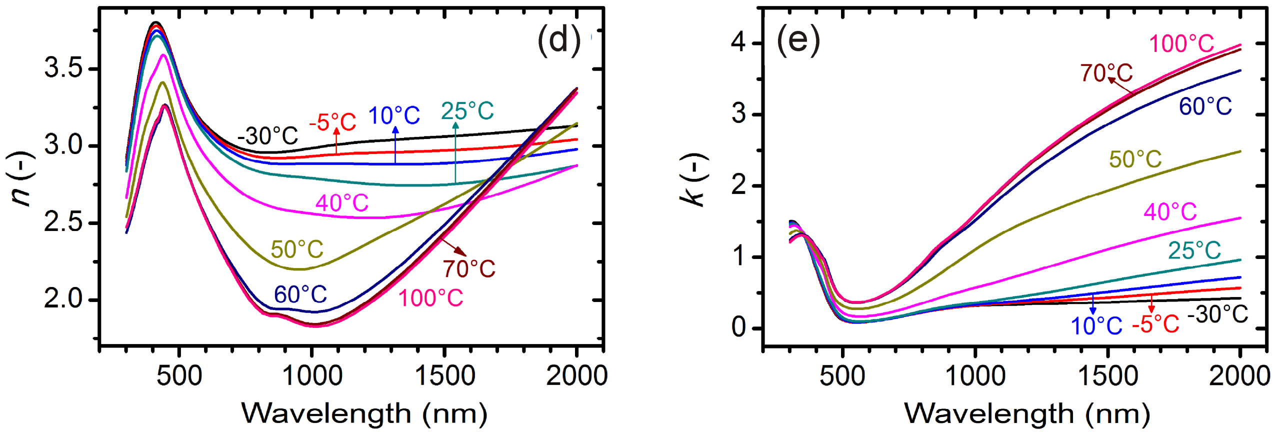
Necessary crystallinity and VO_2 stoichiometry (only one of many possible stoichiometries) $\Rightarrow$ challenging preparation



[Y. Zhang et al., Nanomaterials 11, 338 (2021)]

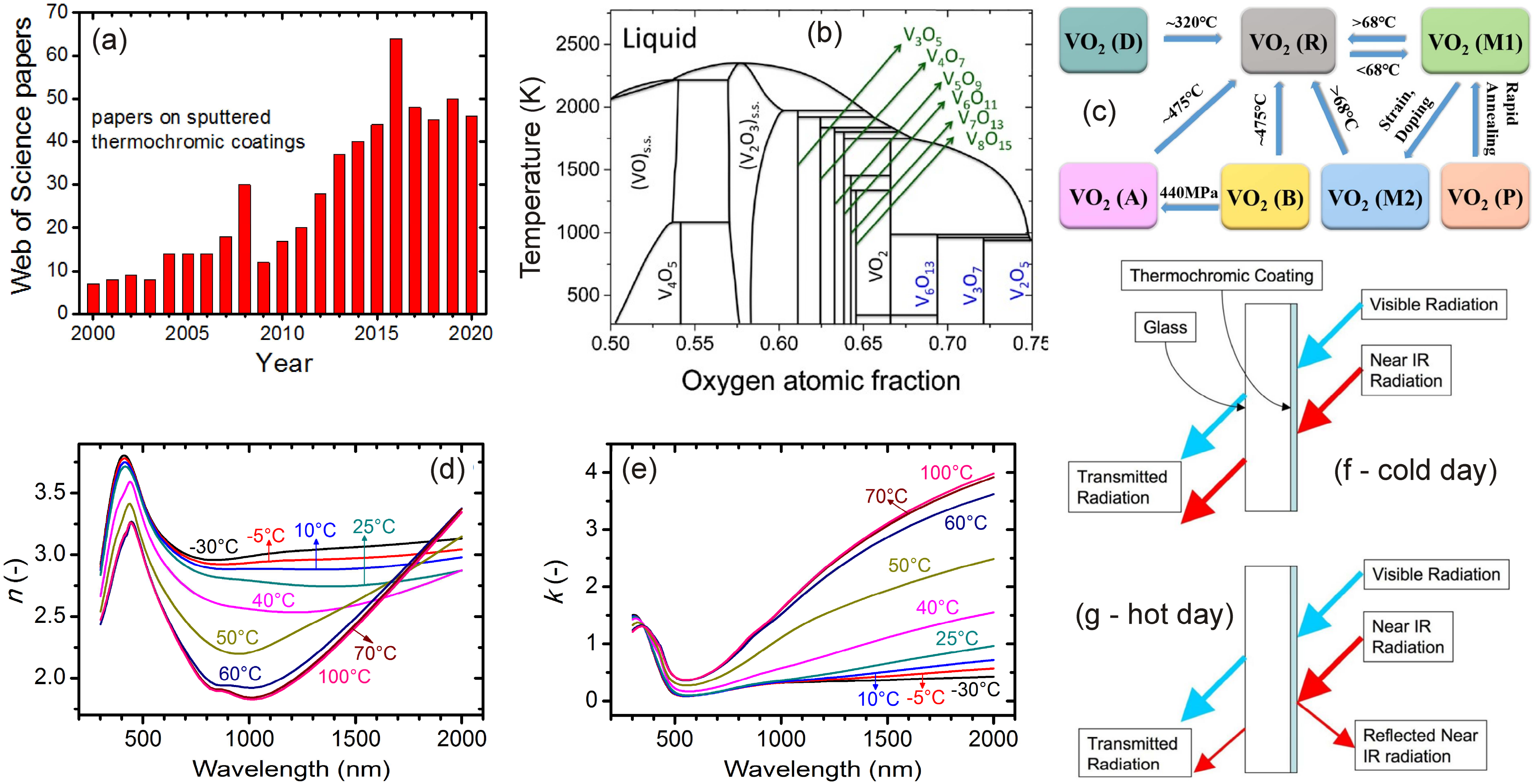
Even at guaranteed crystallinity and stoichiometry, the desired thermochromic phase VO_2(M1⇔R) is only one of many polymorphs (especially at low preparation temperature)





[J. Houska et al., Appl. Surf. Sci. 421, 529 (2017)]

Nevertheless, thermochromic VO_2(M1⇔R) can be prepared (see below) ⇒ strong modulation of free charge carrier concentration and all related properties



[M.E.A. Warwick and R. Binions, J. Solid State Chem. 214, 53 (2014)]

Smart energy-saving windows

- transmittance modulation in the infrared
- preserved transmittance in the visible
  (advantage over market-available electrochromic coatings)

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- refractive index $n(\lambda)$ and extinction coefficient $k(\lambda)$
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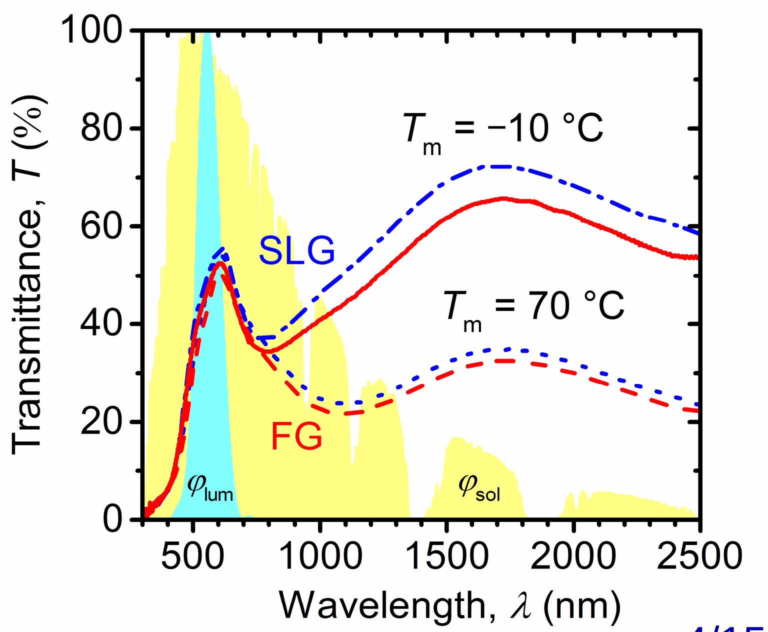
- integral luminous transmittance T_{lum} (& R_{lum} & A_{lum})

$$T_{lum} = \int_{380}^{780} \varphi_{lum}(\lambda)\varphi_{sol}(\lambda)T(\lambda, T_m)d\lambda \Big/ \int_{380}^{780} \varphi_{lum}(\lambda)\varphi_{sol}(\lambda)d\lambda$$



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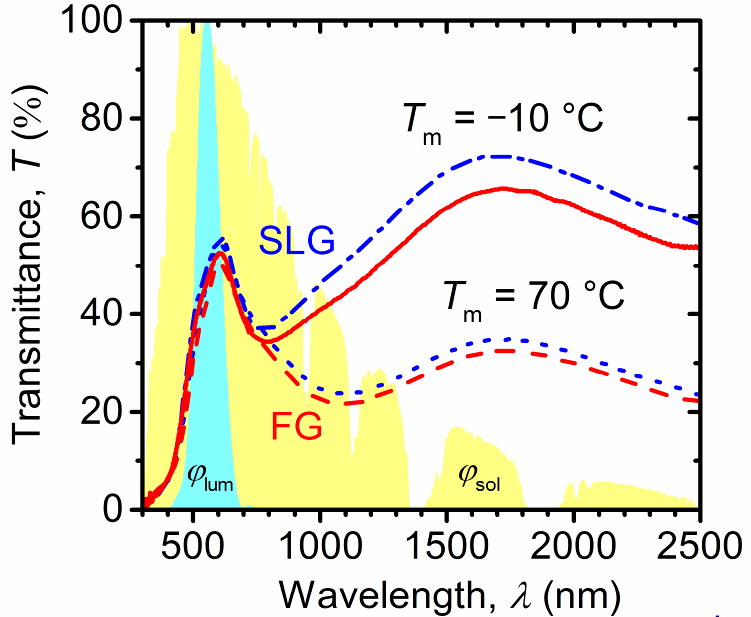

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- resistivity ρ and its modulation ($\Delta\log\rho$ rather than $\Delta\rho$)

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- resistivity ρ and its modulation ($\Delta\log\rho$ rather than $\Delta\rho$)
- color (coordinates in color space such as $L^*a^*b^*$)
- maximum temperature T_{s} during deposition and annealing

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For energy-saving smart windows (not the only application)

- luminous transmittance $T_{\mathrm{lum}} \geq 60\%$

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- maximum substrate temperature $T_{\mathrm{s}} \approx 300°C$ without any substrate bias voltage

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- appealing color in transmission (presently yellowish/brownish)

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- appealing color in transmission (presently yellowish/brownish)
- long-time environmental stability

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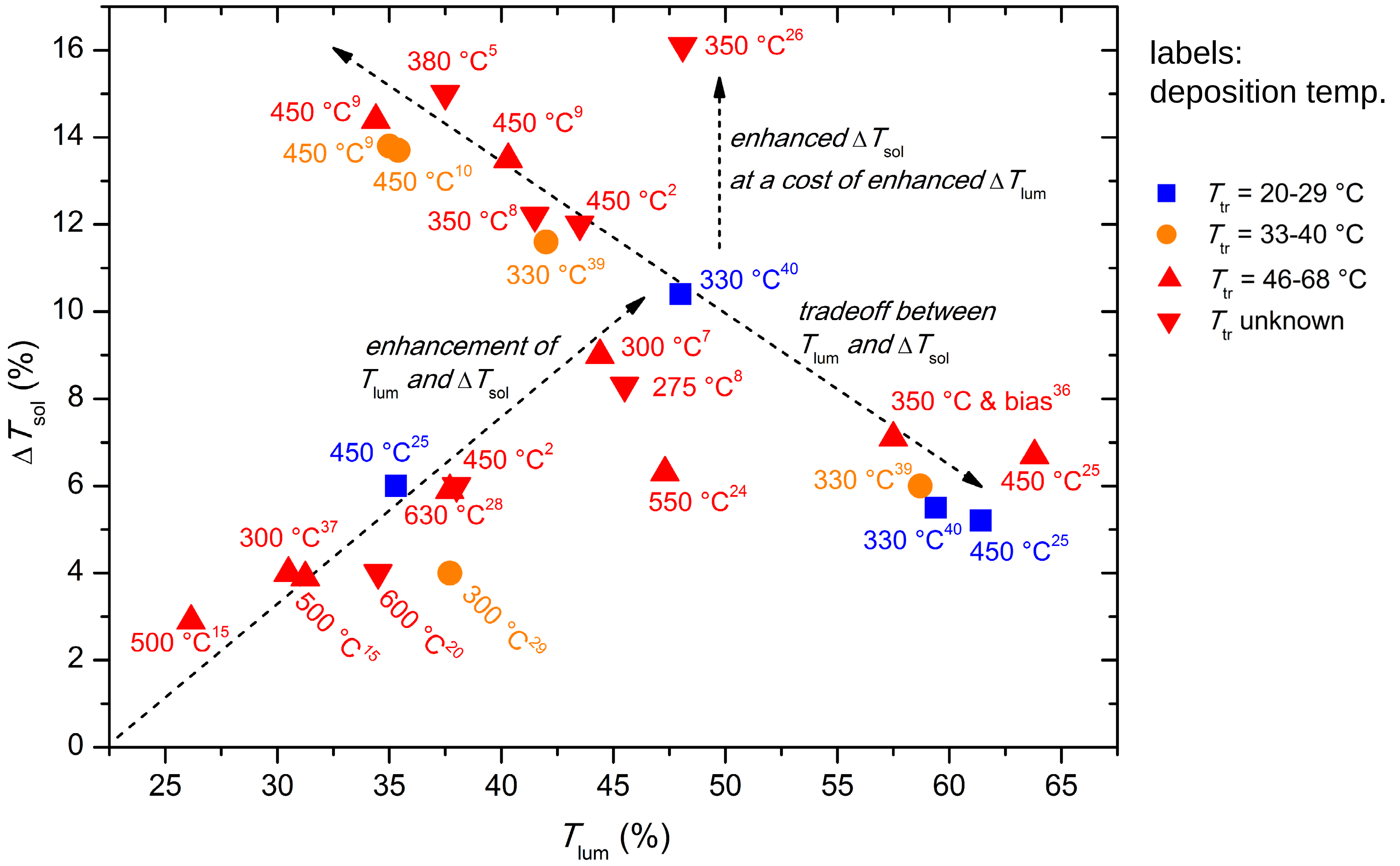
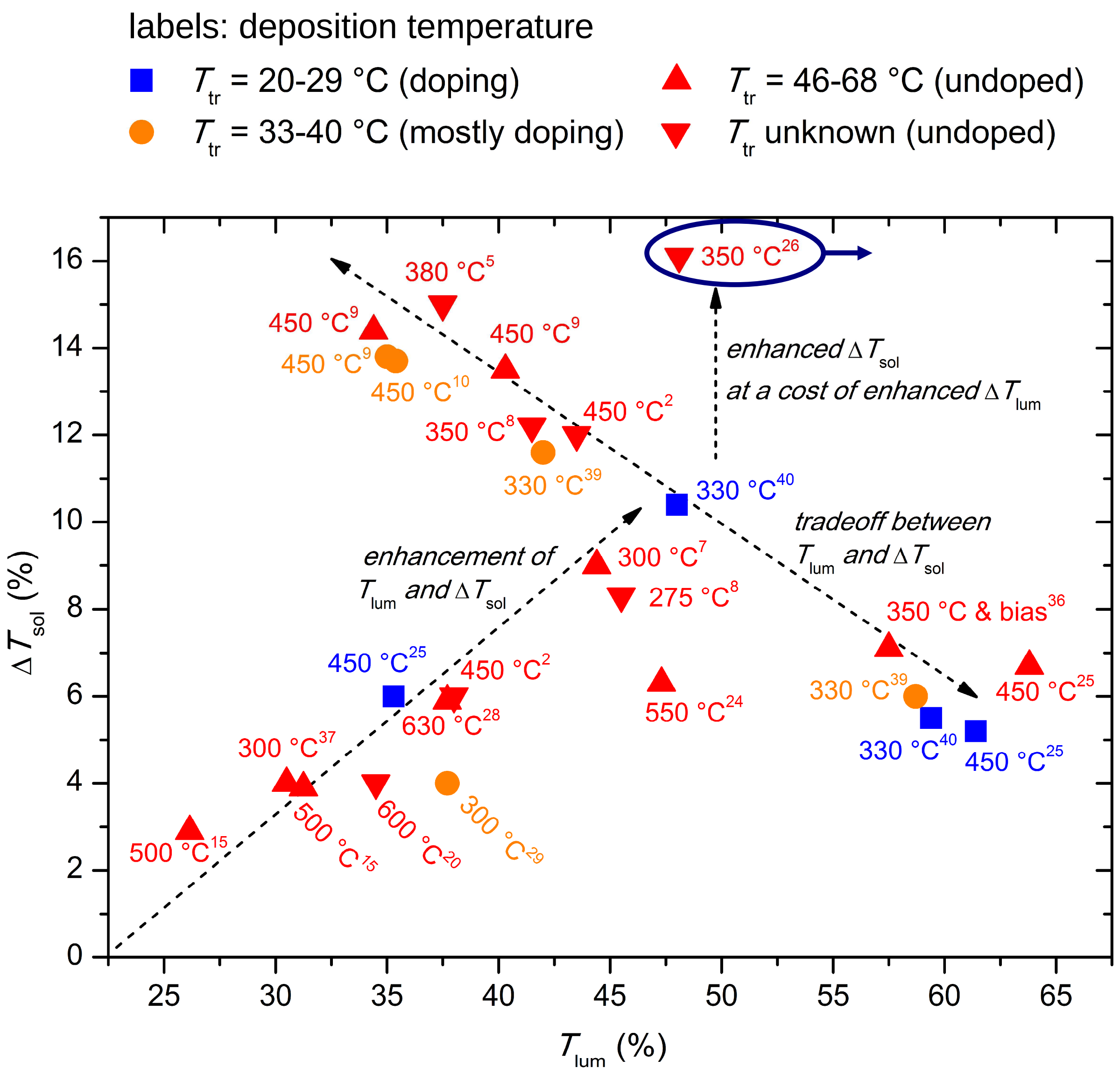
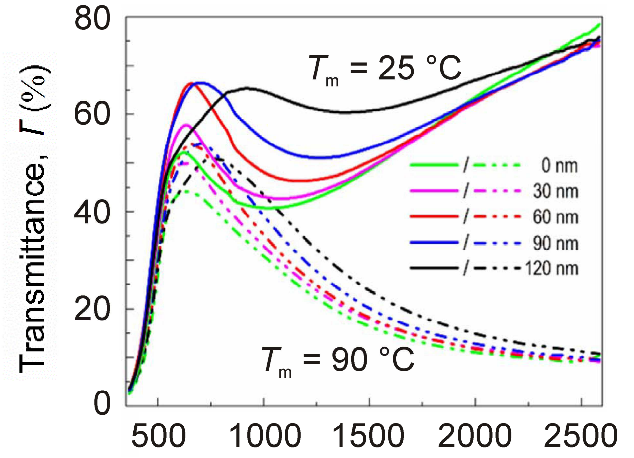
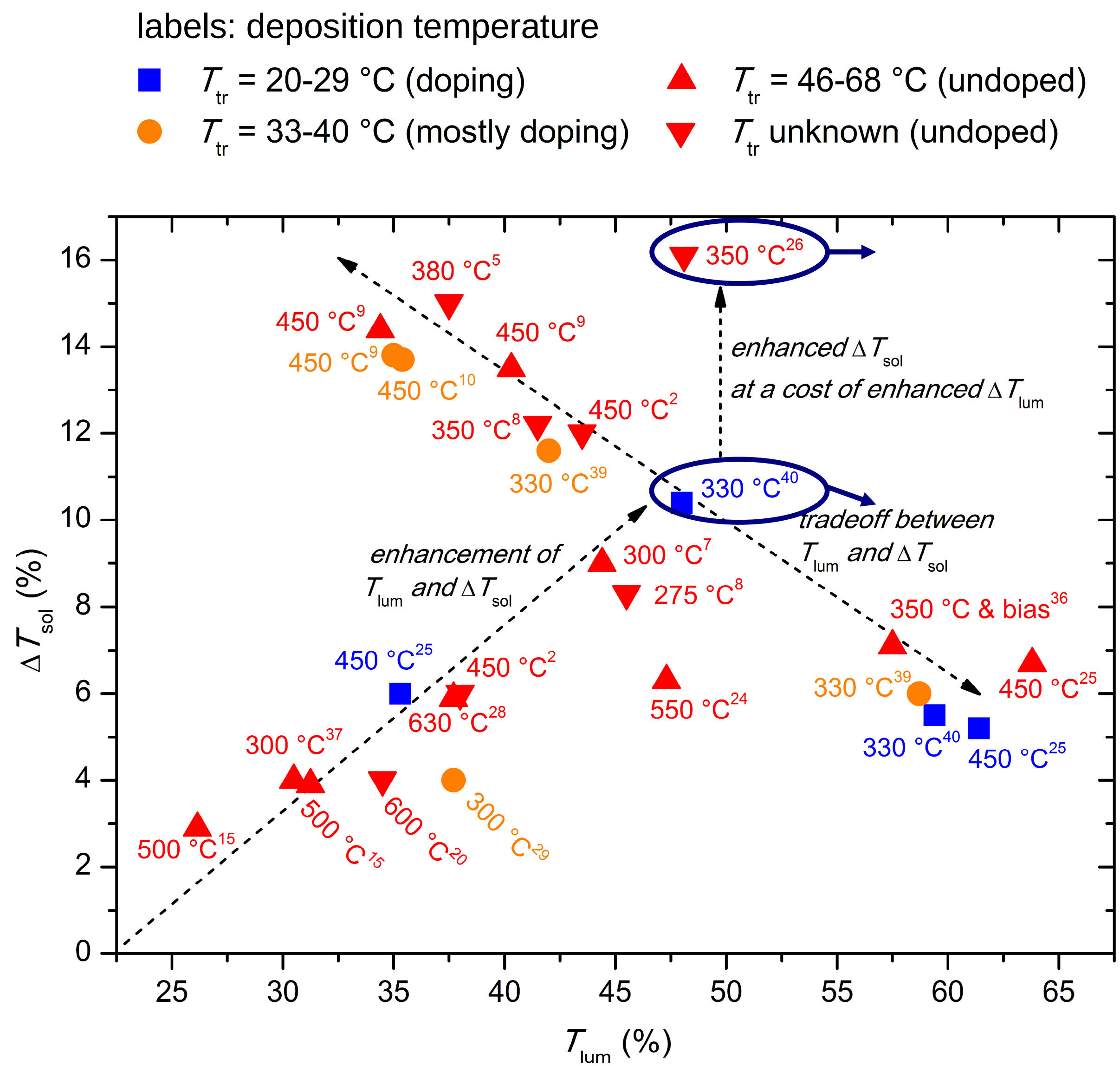


- Development trend leading to enhanced T_{lum} and ΔT_{sol}
- Tradeoff between T_{lum} and ΔT_{sol} of state-of-the-art coatings
- Lowered T_{tr} to ≈20°C & T_s to ≈300 °C at preserved T_{lum} & ΔT_{sol}

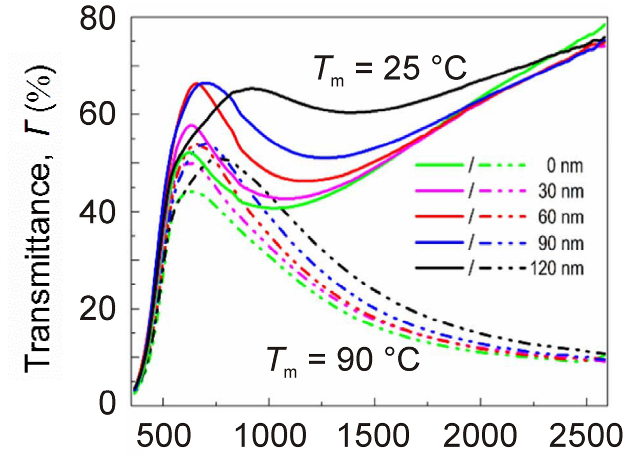




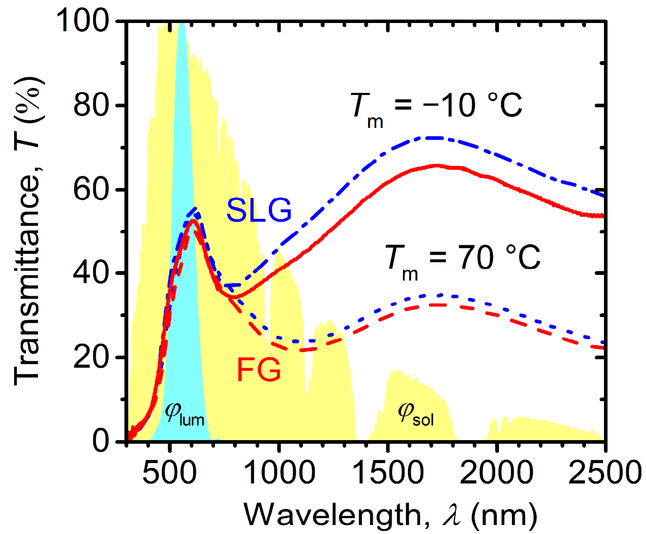
- Some VO_2-based coatings: switching also in the visible



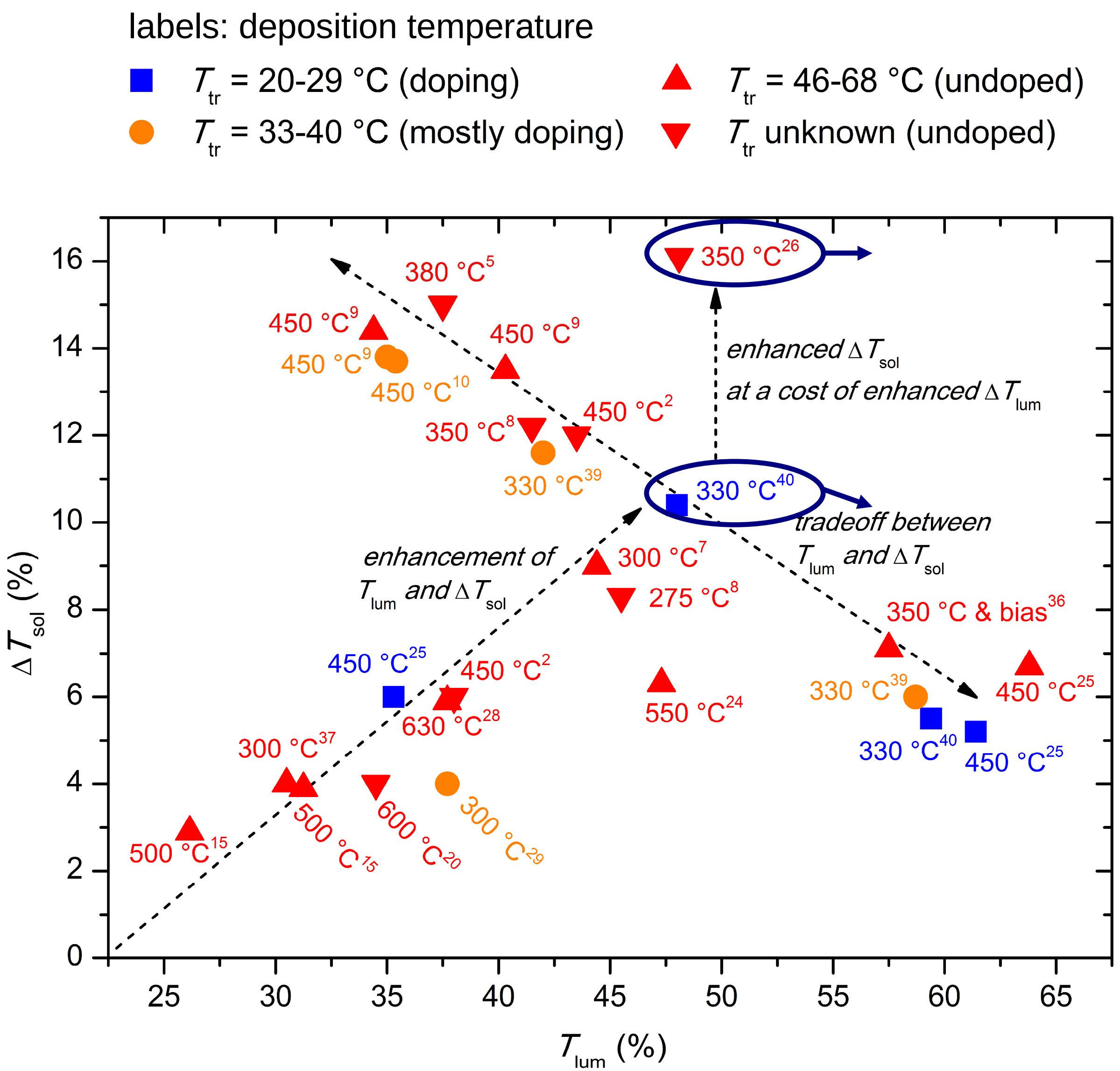
[T. Chang et al., Nano Energy 44, 256 (2018)]



[T. Barta et al., Coatings 10, 1258 (2020)]



- Some VO_2-based coatings: switching also in the visible
- Other VO_2-based coatings: switching only in the infrared



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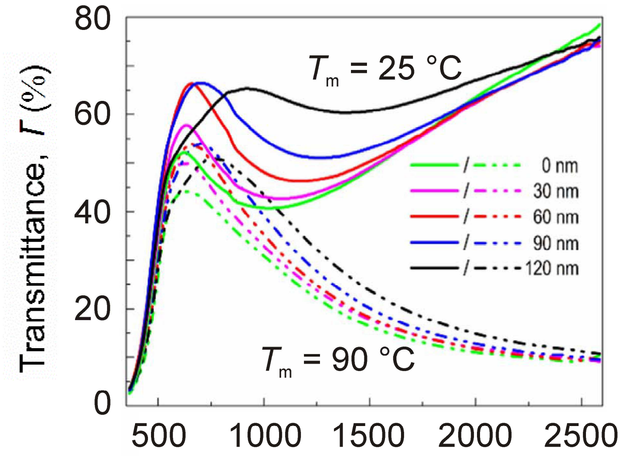

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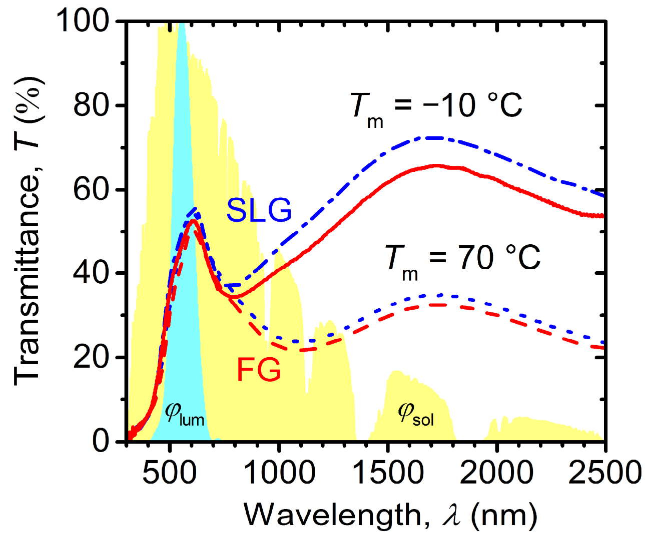

- Some VO_2-based coatings: switching also in the visible
- Other VO_2-based coatings: switching only in the infrared
- (speculation mode activated) Role of exact $VO_{2\pm x}$ composition?

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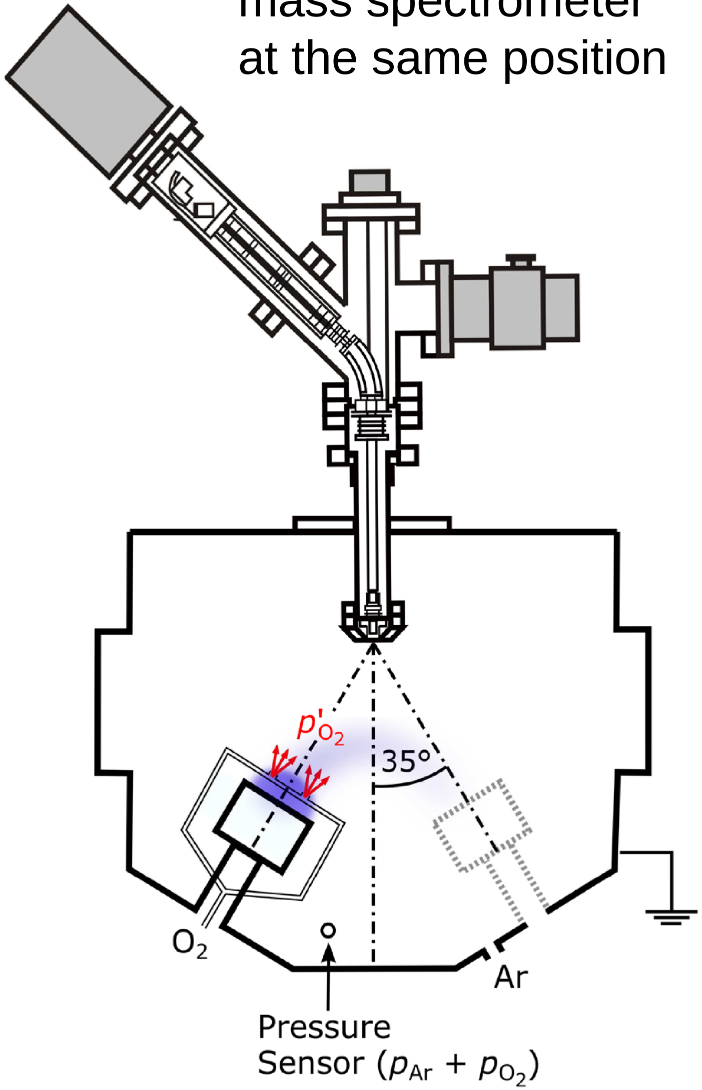
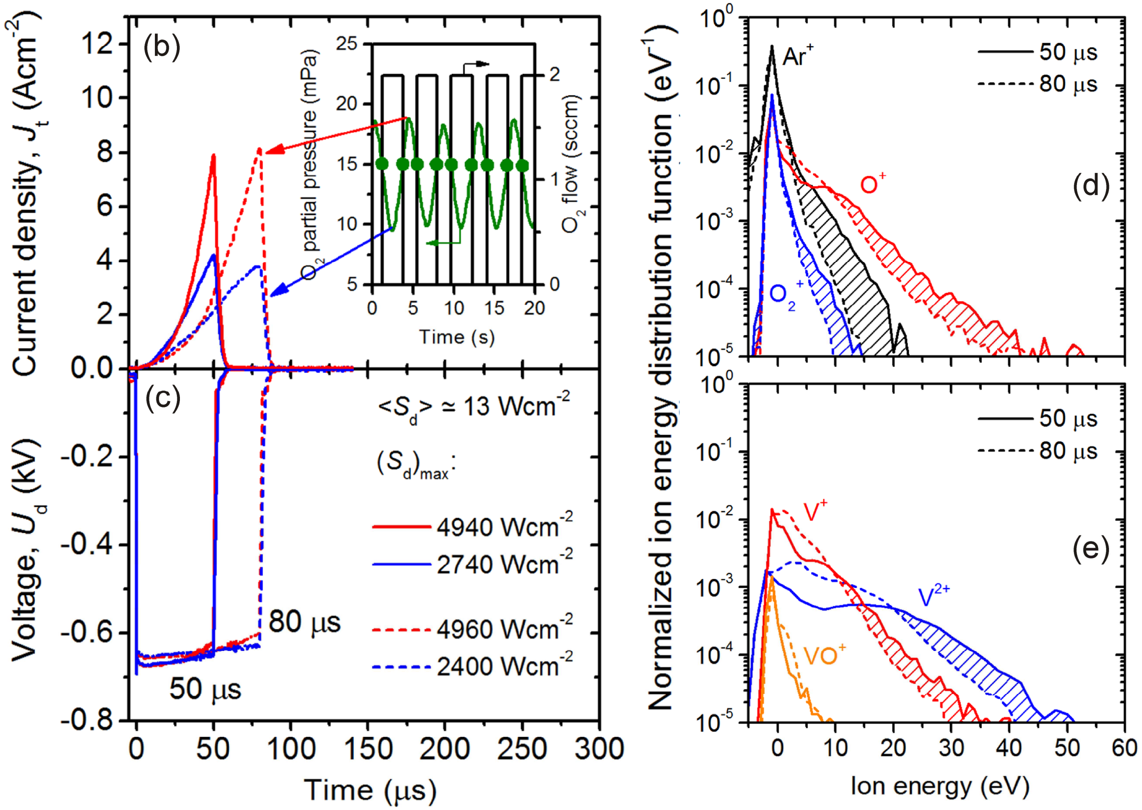


Only one deposition technique previously fulfilled all the key requirements (T_{lum}, ΔT_{sol}, T_{tr}, T_s)

Let's see the core of this technique: **full utilization of the advantages of HiPIMS** (not just using HiPIMS) **of VO_2 with pulsed O_2 flow control**

[J. Vlcek et al., J. Phys. D Appl. Phys. 50, 38LT01 (2017)]
[J. Vlcek et al., J. Phys. D Appl. Phys. 52, 025205 (2019)]



HiPIMS:

(≤5 kWcm^{-2} in a pulse at 13 Wcm^{-2} in a period and 1% duty cycle)

⇓

bombardment by highly ionized fluxes with many metal ions

⇓

crystallinity at low T_s **= 300 °C** on glass substrate (250 °C on crystalline substrate)

[J. Vlcek et al., J. Phys. D Appl. Phys. 50, 38LT01 (2017)]
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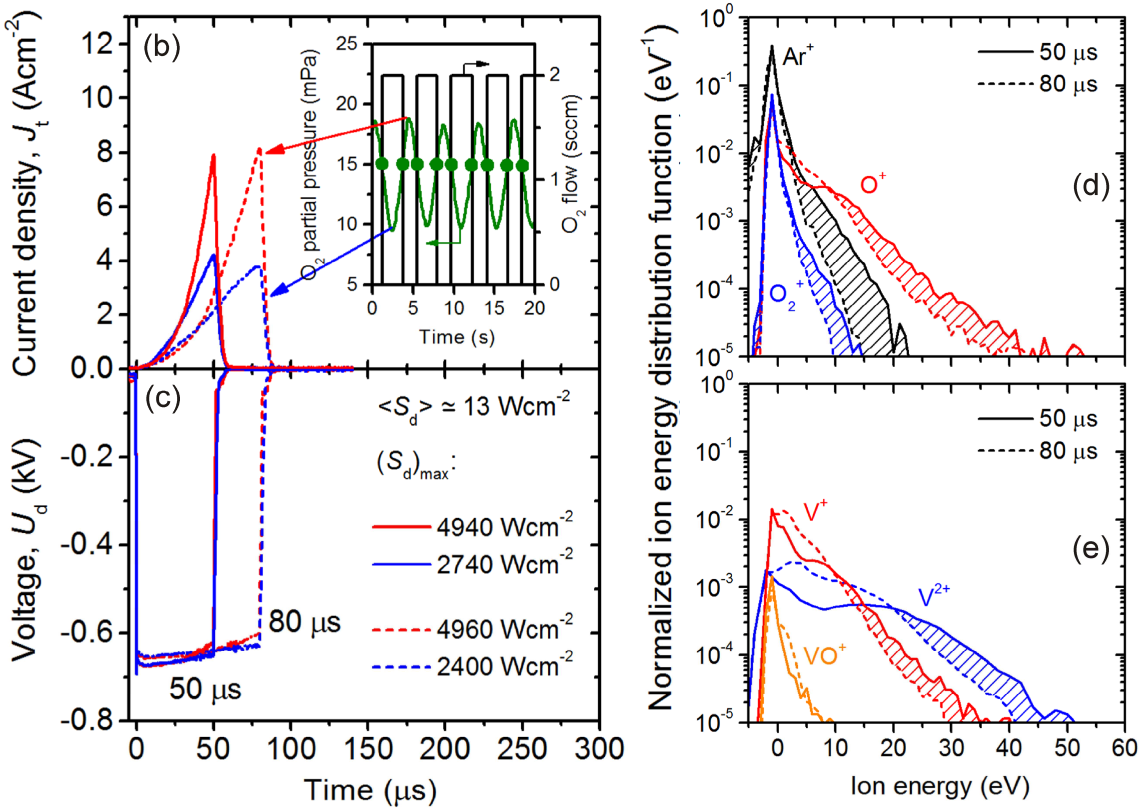


Pulsed O_2 flow control:

O_2 partial pressure or sputtering current compared with its preset critical value

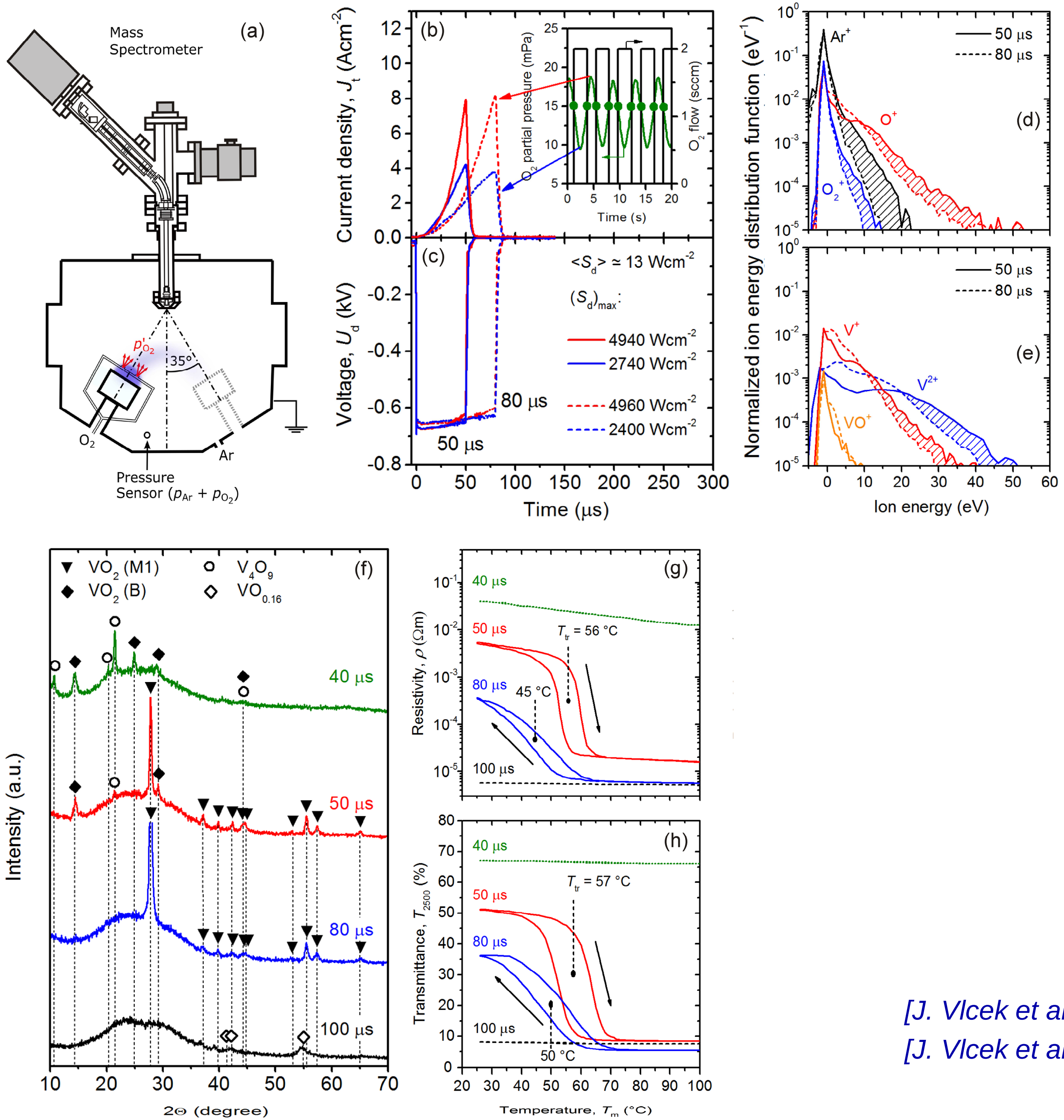
⇓

O_2 flux opened and closed by a feedback logical controller

⇓

desired VO_2 stoichiometry

[J. Vlcek et al., J. Phys. D Appl. Phys. 50, 38LT01 (2017)]
[J. Vlcek et al., J. Phys. D Appl. Phys. 52, 025205 (2019)]

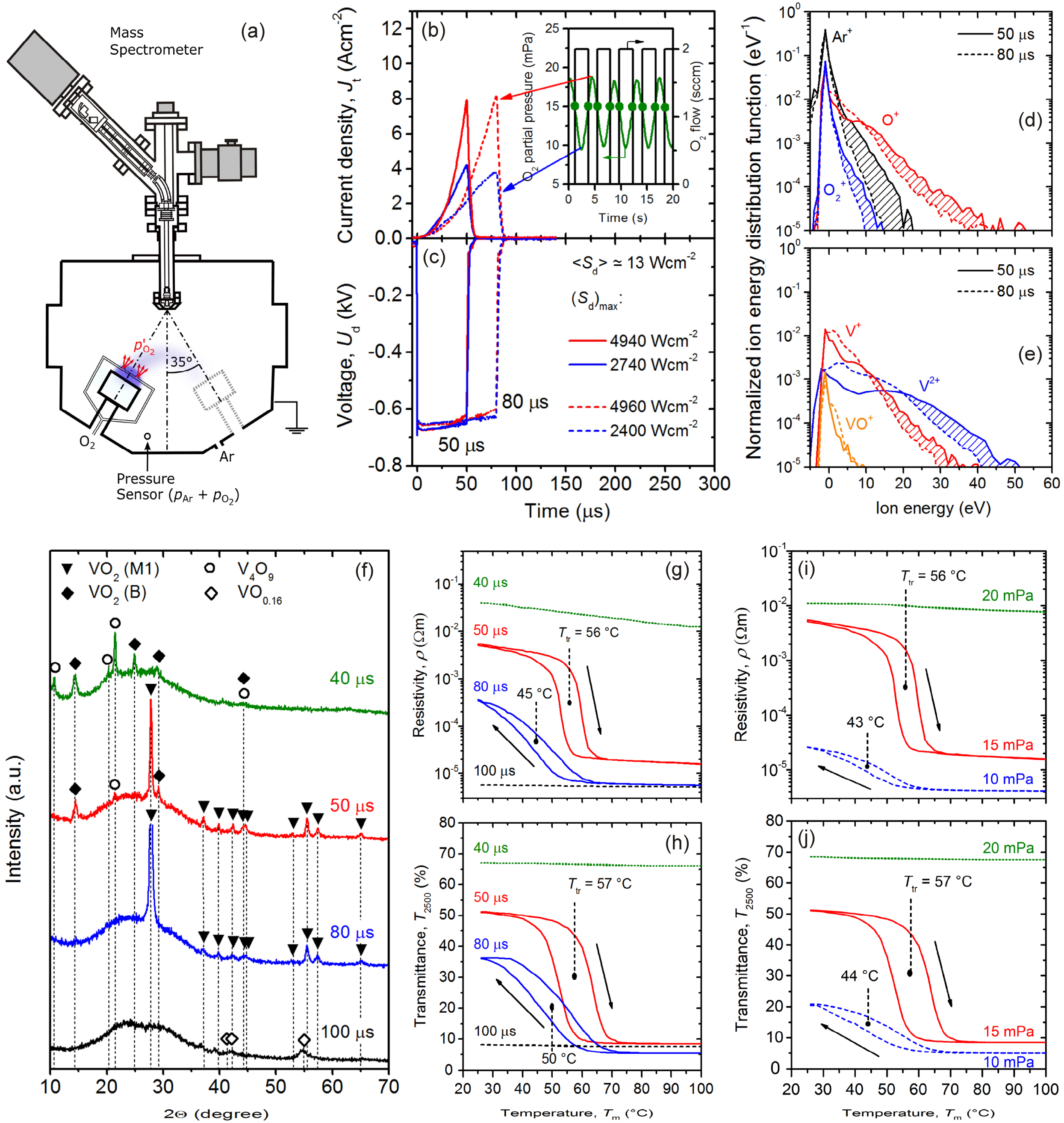


Two main control parameters

(1) **voltage pulse duration, t_{on}**

higher energy delivered into films and higher [O]/[V] ratio at shorter t_{on}

[J. Vlcek et al., J. Phys. D Appl. Phys. 50, 38LT01 (2017)]
[J. Vlcek et al., J. Phys. D Appl. Phys. 52, 025205 (2019)]



Two main control parameters

(1) **voltage pulse duration, t_{on}**

higher energy delivered into films and higher [O]/[V] ratio at shorter t_{on}

(2) **critical O_2 partial pressure, $(p_{ox})_{cr}$**

narrow (≈ ±10%) $(p_{ox})_{cr}$ window at proper t_{on}, closes to zero at improper t_{on}

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I. Introduction and background

II. Quantities of interest and criteria of success

III. Properties and sputtering of thermochromic VO_2

IV. Ways to improve the coating characteristics

A. Suitable doping elements

B. Suitable materials of antireflection layers

C. Design of multilayers with optimized ΔT_{sol} and T_{lum}

D. Design of multilayers with optimized ΔT_{sol} and color

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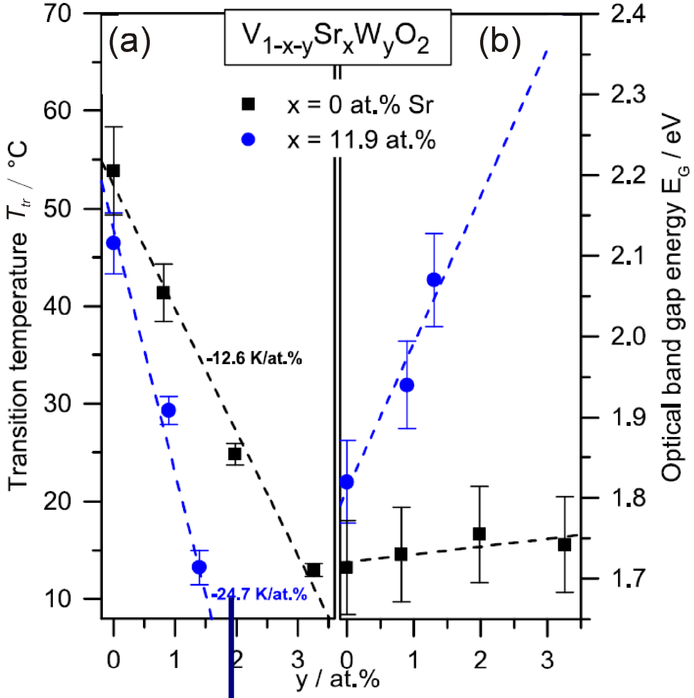


(c)

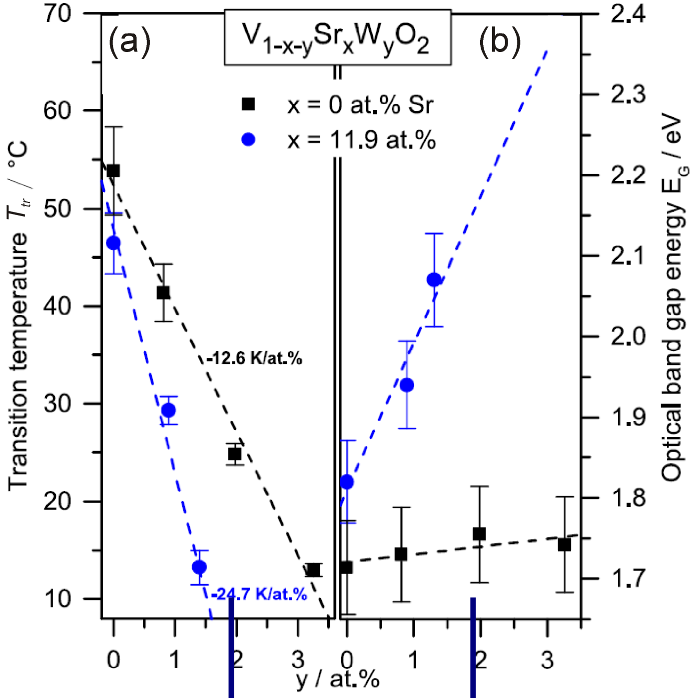
Dopant	Group	Reported T_{tr} gradients	Source
W	VI B	-13 to -22 °C/at.%	papers dealing with sputtering[13,19,25,39,40]
W	VI B	-19 to -27 °C/at.%	ab-initio calculations[80]
W	VI B	-7 to -35 °C/at.%	literature overview (focused on W)[88]
Mo	VI B	-6 to -23 °C/at.%	
Cr	VI B	+1 °C/at.%	
Nb	V B	-8 °C/at.%	literature overview (broad)[91]
Ti	IV B	0 °C/at.%	
Mg	II A	-2 to -3 °C/at.%	
F	VII A	-11 °C/at.%	

[M.K. Dietrich et al., Appl. Phys. Lett. 110, 141907 (2017)]

Two reasons to dope VO_2

(1) shift T_{tr} from 68°C (bulk) or ≈60°C (films) to ≈20°C

- disorder by large atoms + one extra electron ⇒ W, Mo
- linear dependence between [W] and T_{tr}
- however, various gradients (our data -15 to -19 °C/at.%)



[M.K. Dietrich et al., Appl. Phys. Lett. 110, 141907 (2017)]

(c)

Dopant	Group	Reported T_{tr} gradients	Source
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F	VII A	-11 °C/at.%	

Two reasons to dope VO_2

(1) shift T_{tr} from 68°C (bulk) or ≈60°C (films) to ≈20°C
- disorder by large atoms + one extra electron ⇒ W, Mo
- linear dependence between [W] and T_{tr}
- however, various gradients (our data -15 to -19 °C/at.%)

(2) manipulate transmittance and color
- widening of optical gap by Mg (large gradient), Ca, Sr, Ba
- doping on O sublattice by F (CH_3F or CF_4 in plasma)

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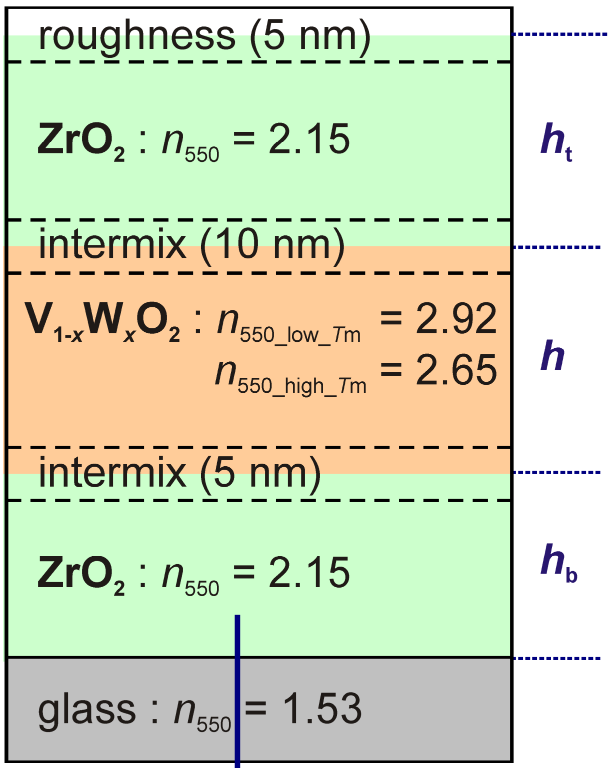
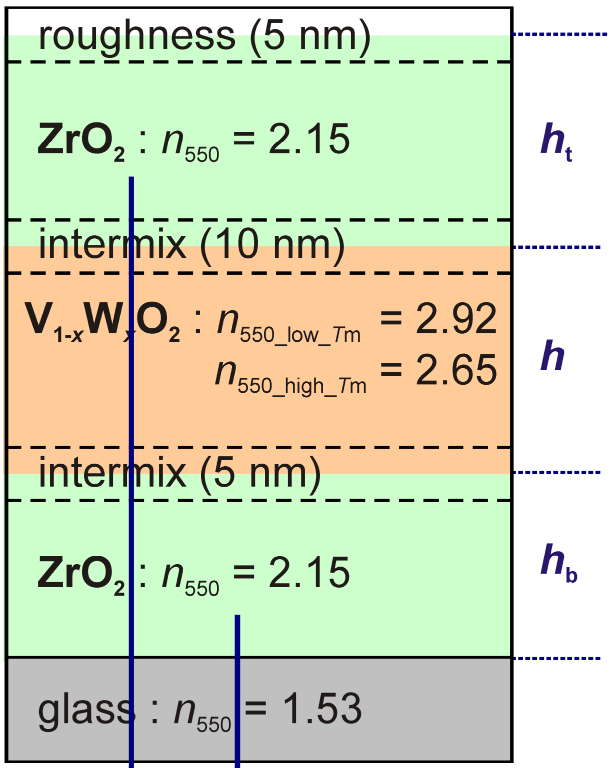
(a) Example of coating design[39]



Bottom layer
- antireflection ⇒ n_{550} close to $\sqrt{(n_{550\_VO2} \times n_{550\_glass})}$
- template further improving the VO_2 crystallinity

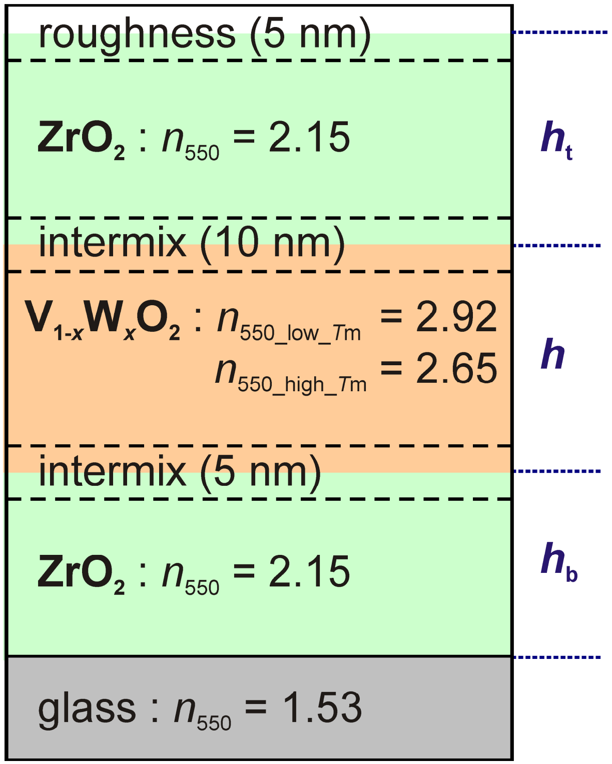
(a) Example of coating design[39]



Bottom layer
- antireflection ⇒ n_{550} close to $\sqrt{(n_{550\_VO2} \times n_{550\_glass})}$
- template further improving the VO_2 crystallinity

Top layer
- antireflection ⇒ n_{550} close to $\sqrt{(n_{550\_VO2} \times n_{550\_air})}$
- hard protective layer

(a) Example of coating design[39]



(b) Materials of AR-layers

Material	n_{550} allowing functionality of bottom AR-layer	Potential as crystalline template	n_{550} allowing functionality of top AR-layer	Protective because harder than VO_2	Wide band gap guaranteeing low k_{550}
ZrO_2	yes	yes	yes	yes	yes
SiO_2	too low	irrelevant due to n_{550}	yes	no	yes
Al_2O_3	too low	irrelevant due to n_{550}	yes	comparable	yes
Cr_2O_3	yes	yes	high but acceptable	yes	no
SnO_2	yes	yes	yes	no	no
TiO_2	too high	excellent	too high	irrelevant due to n_{550}	really no

Bottom layer ▪ antireflection + template

Top layer ▪ antireflection + protective

Complementary (dis)advantages, including (non)zero extinction coeffcient, of various candidate oxides and other materials

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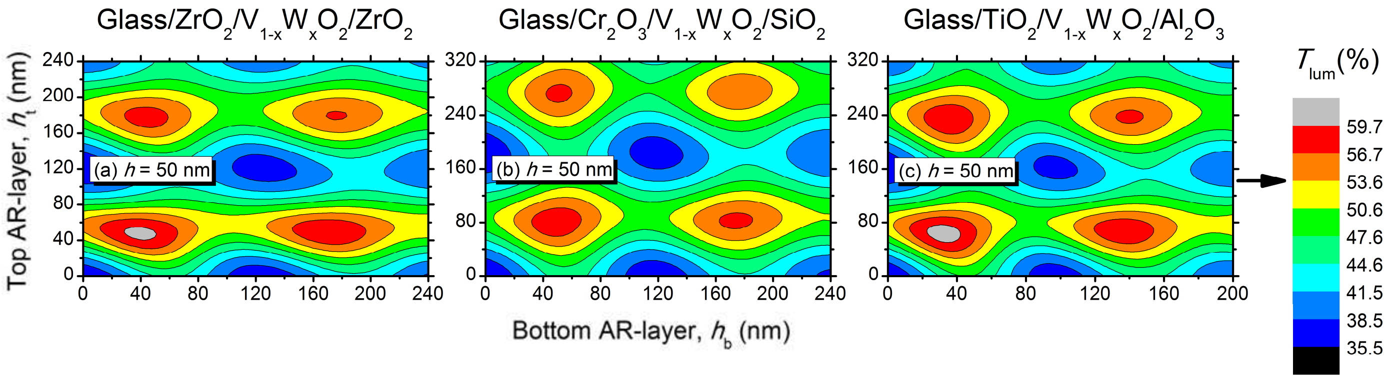
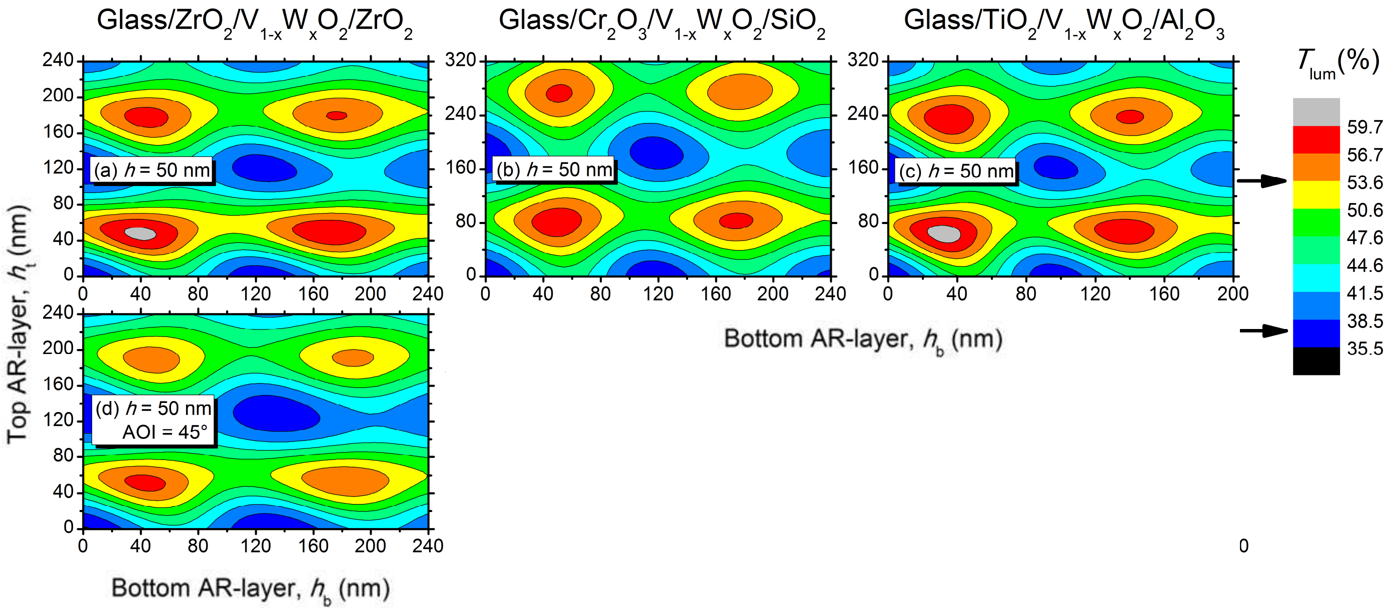


[J. Houska, Sol. Energy Mater. Sol. Cells 191, 365 (2019)]

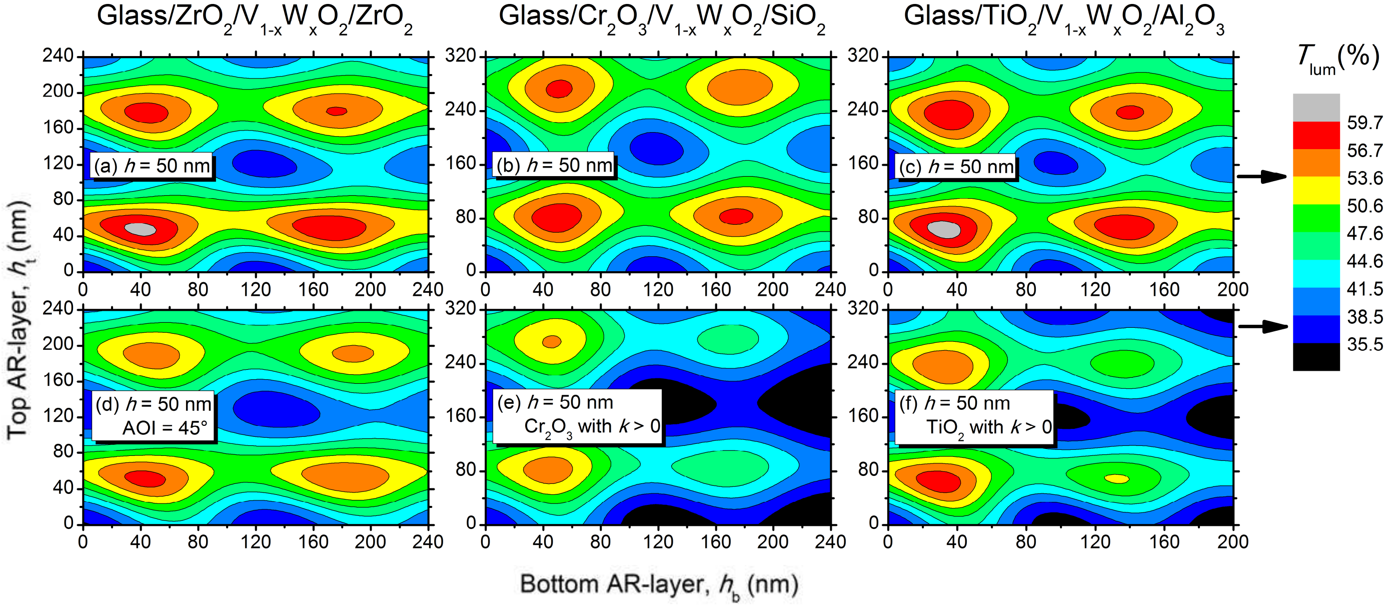
1st-order and 2nd-order maxima of T_{lum} for 3 different designs



[J. Houska, Sol. Energy Mater. Sol. Cells 191, 365 (2019)]

1st-order and 2nd-order maxima of T_{lum} for 3 different designs

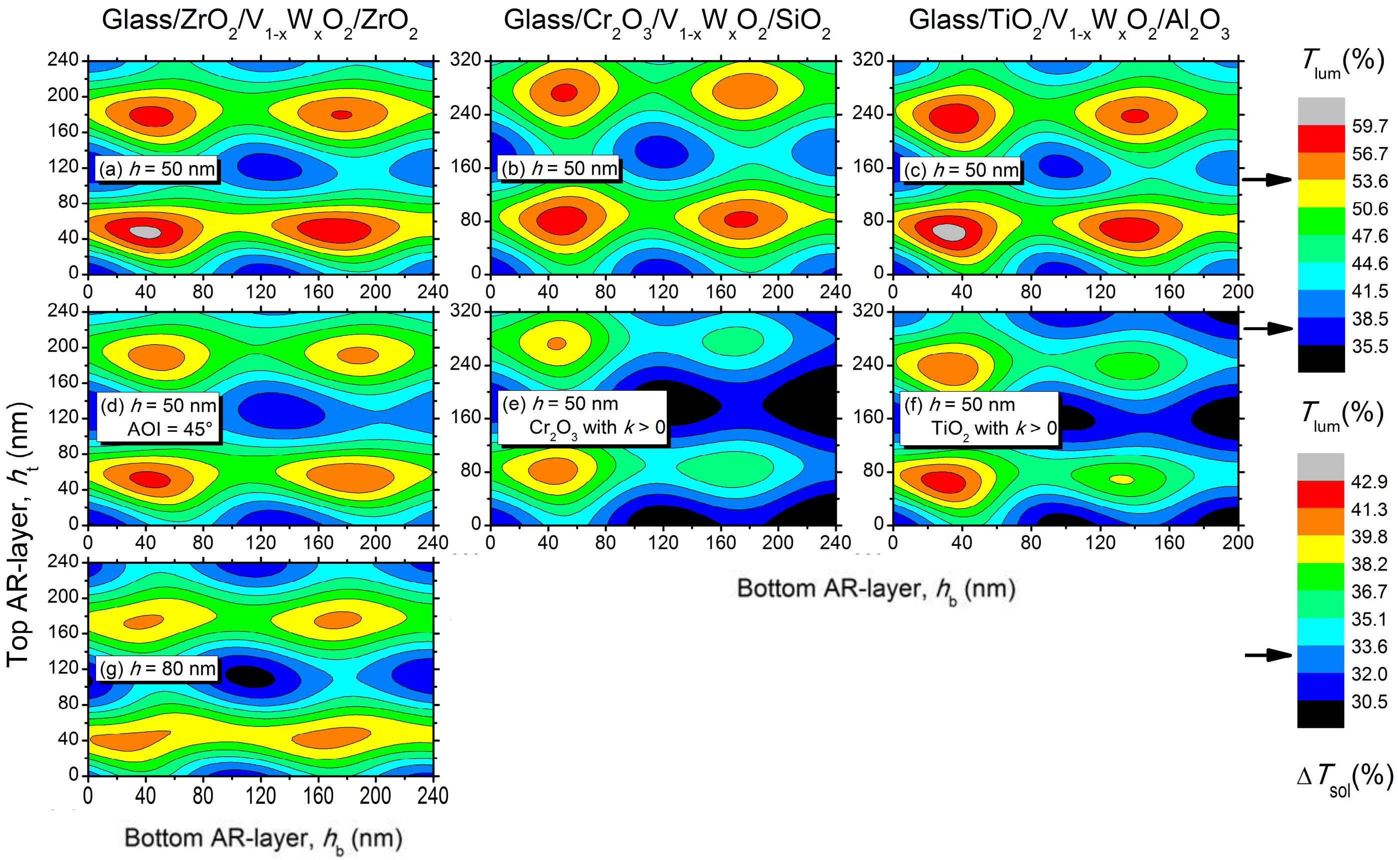
- Angle of incidence AOI = 45° instead of 0°: refraction toward normal ⇒ only slight shift



[J. Houska, Sol. Energy Mater. Sol. Cells 191, 365 (2019)]

1st-order and 2nd-order maxima of T_{lum} for 3 different designs

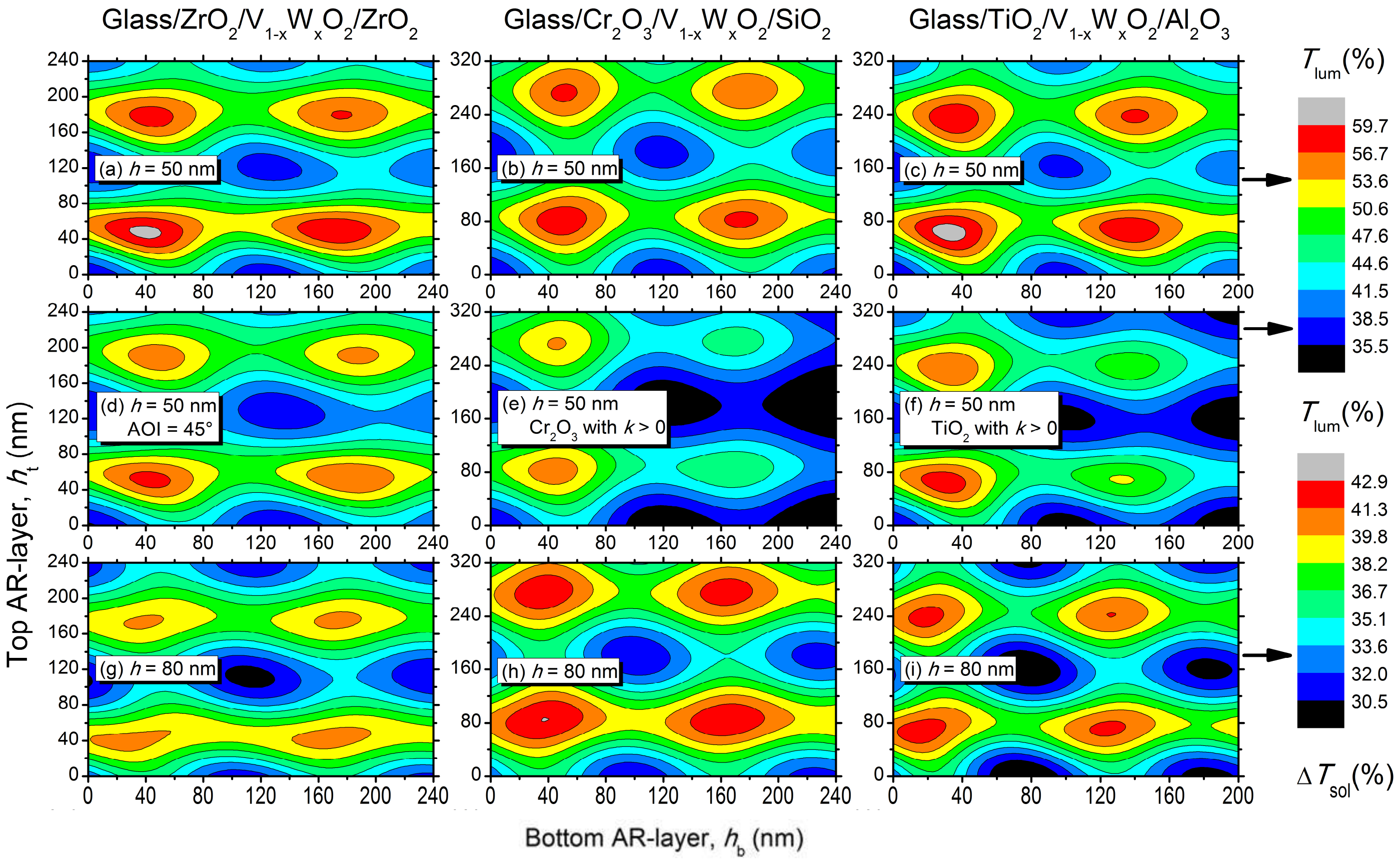
- Angle of incidence AOI = 45° instead of 0°: refraction toward normal ⇒ only slight shift
- Realistic $k_{550} > 0$ of Cr_2O_3 & TiO_2: 2nd-order maxima of T_{lum} are lower



[J. Houska, Sol. Energy Mater. Sol. Cells 191, 365 (2019)]

VO_2 thickness h = 80 nm instead of h = 50 nm

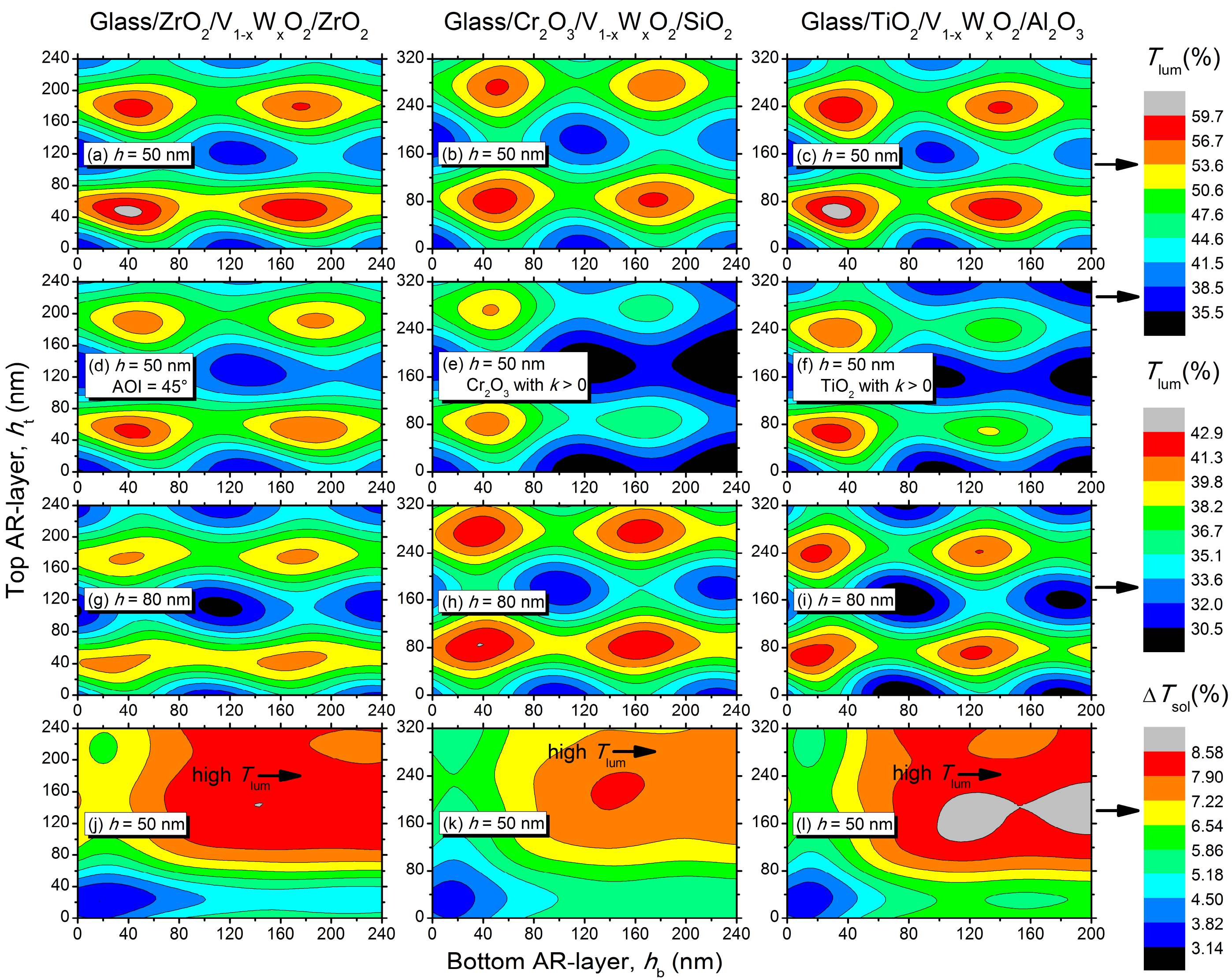
- ZrO_2, SiO_2, Al_2O_3 (n_{550} far from VO_2): weak effect on optimum AR-layer thickness



[J. Houska, Sol. Energy Mater. Sol. Cells 191, 365 (2019)]

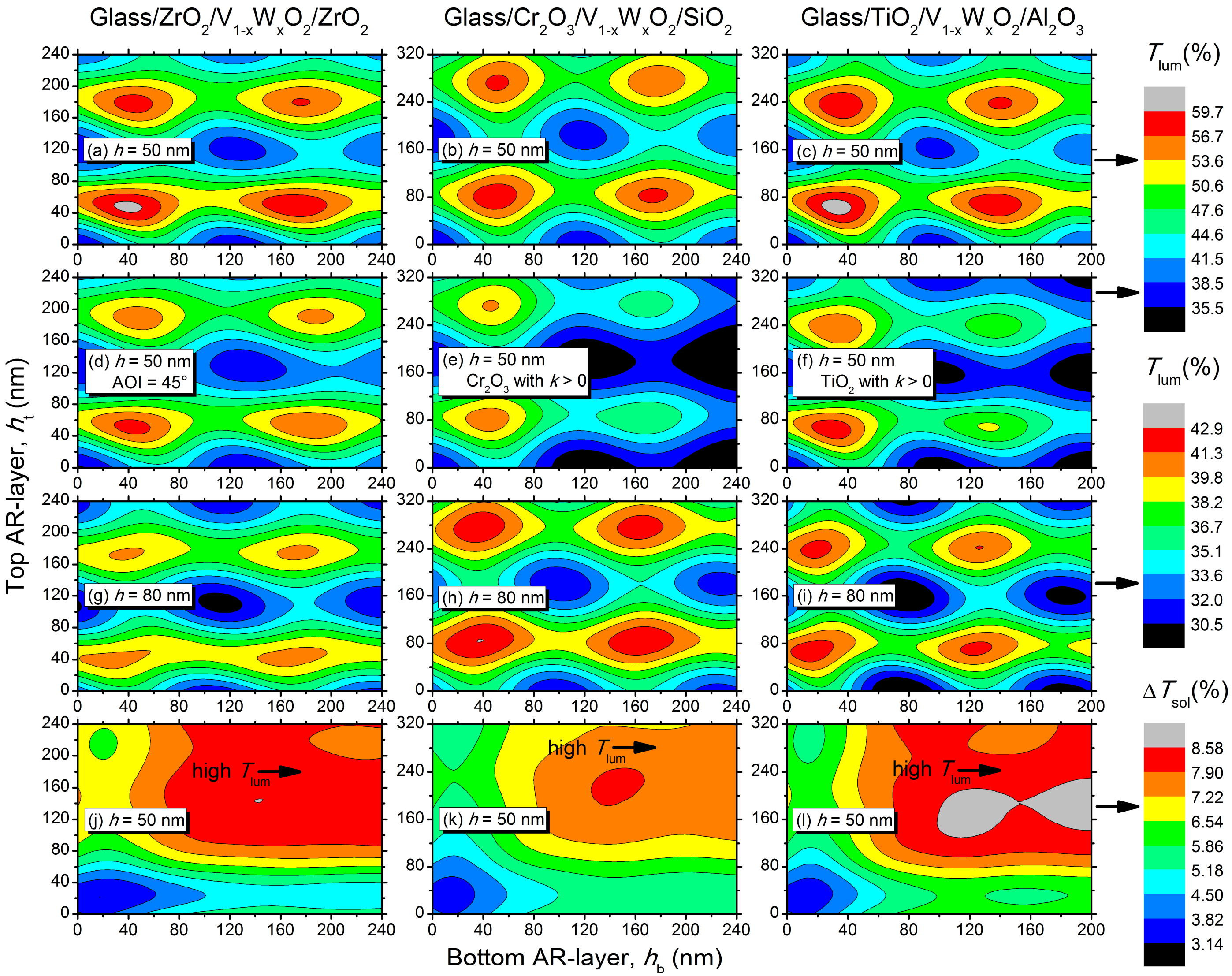
VO_2 thickness h = 80 nm instead of h = 50 nm

- ZrO_2, SiO_2, Al_2O_3 (n_{550} far from VO_2): weak effect on optimum AR-layer thickness
- Cr_2O_3, TiO_2 (n_{550} closer to VO_2): negative correlation with optimum AR-layer thickness



[J. Houska, Sol. Energy Mater. Sol. Cells 191, 365 (2019)]

- **1st-order maxima** in the visible:
  nothing special in the infrared, high T_{lum} but low ΔT_{sol}



[J. Houska, Sol. Energy Mater. Sol. Cells 191, 365 (2019)]

- **1st-order maxima** in the visible:
  nothing special in the infrared, high T_{lum} but low ΔT_{sol}
- **2nd-order maxima** in the visible:
  1st-order maxima in the infrared, high T_{lum} and high ΔT_{sol}

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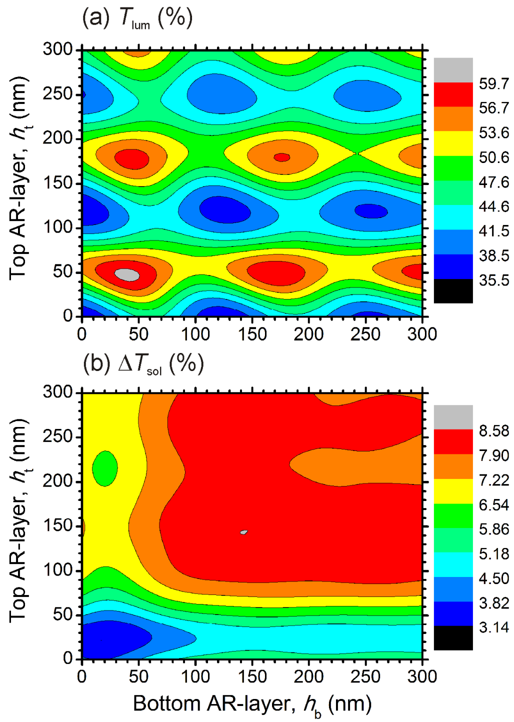
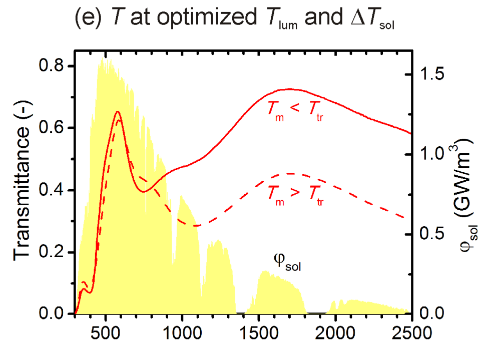


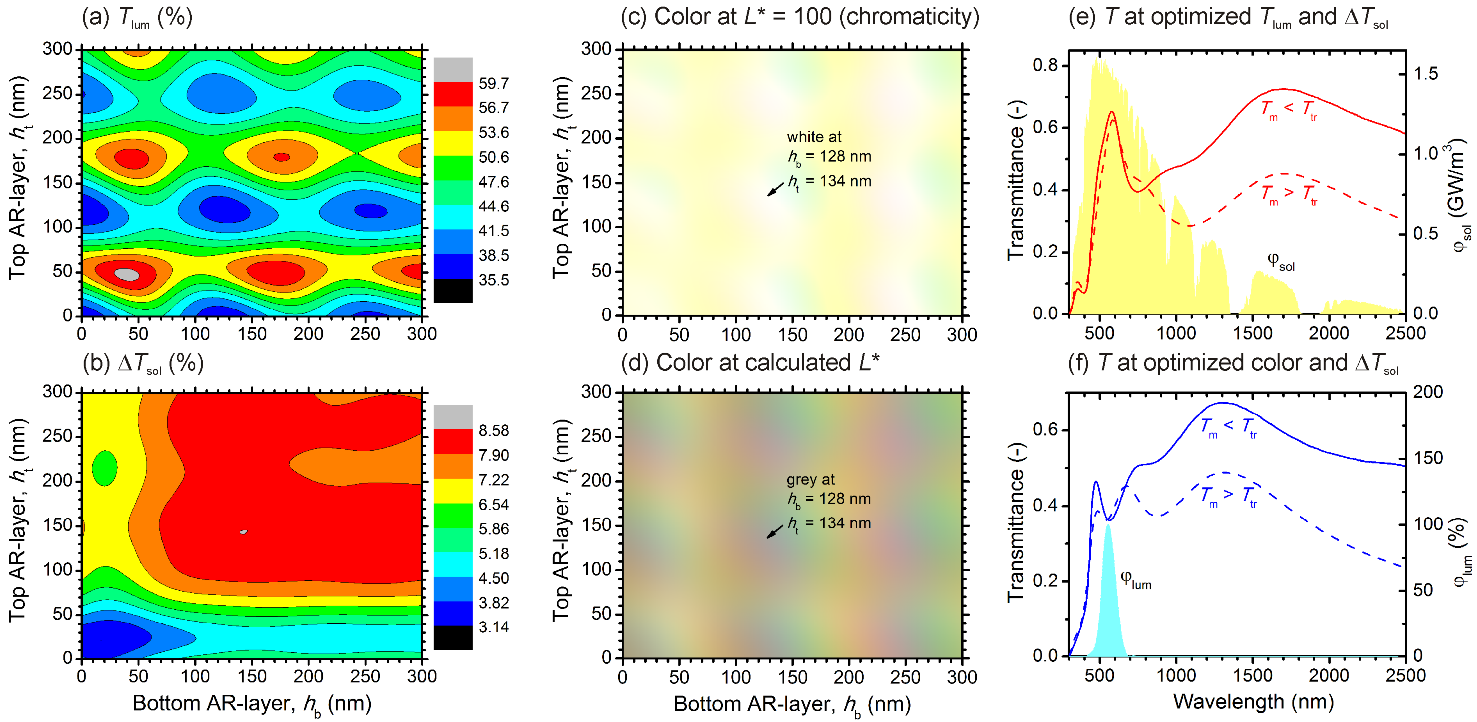


shown for
ZrO_2 (h_t)
$V_{1-x}W_xO_2$ (h)
ZrO_2 (h_b)

h = 50 nm
if not stated
otherwise

[J. Houska, Sol. Energy Mater. Sol. Cells 230, 111210 (2021)]

High T_{lum} & ΔT_{sol} at $h_{b,t} \approx 180$ nm
2nd-order maxima of $T(\lambda)$ in the visible $\Rightarrow$
1st-order maxima of $T(\lambda)$ in the infrared



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ZrO_2 (h_t)
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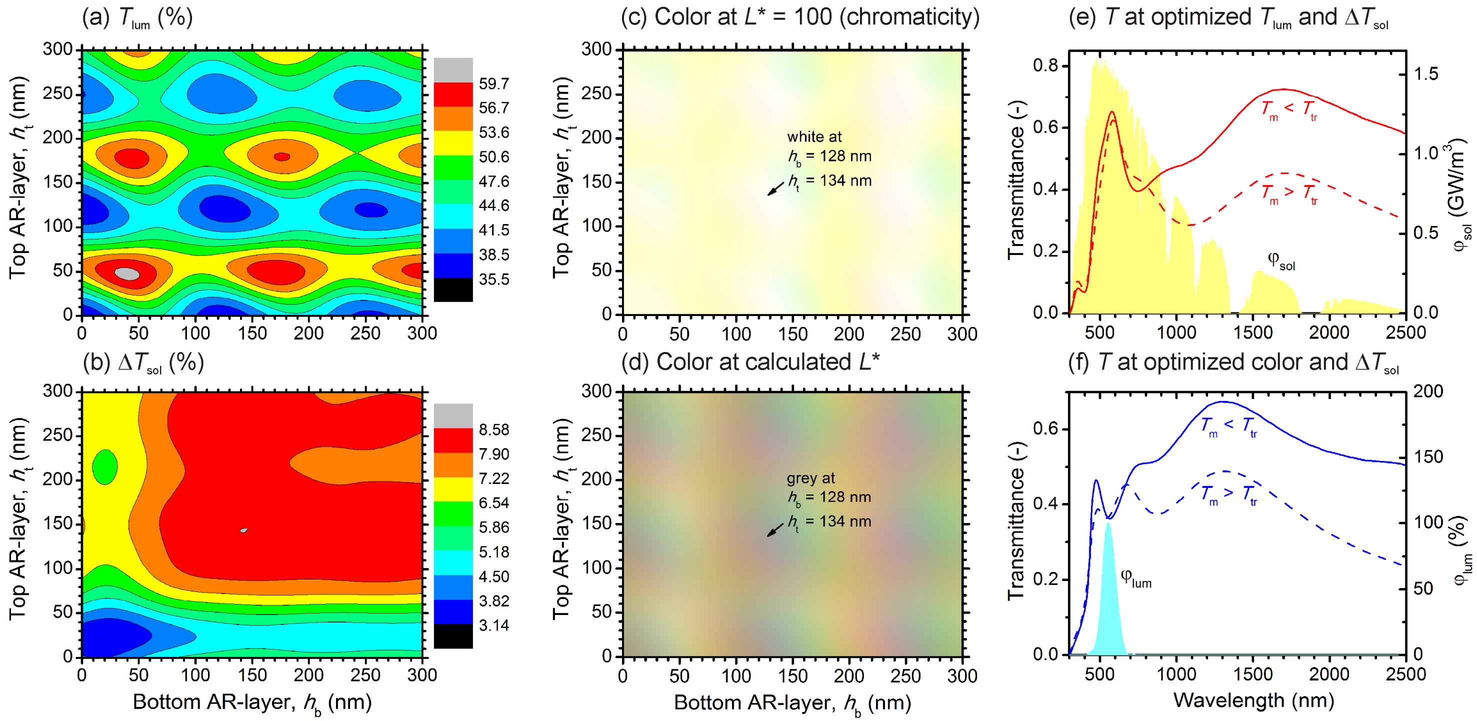
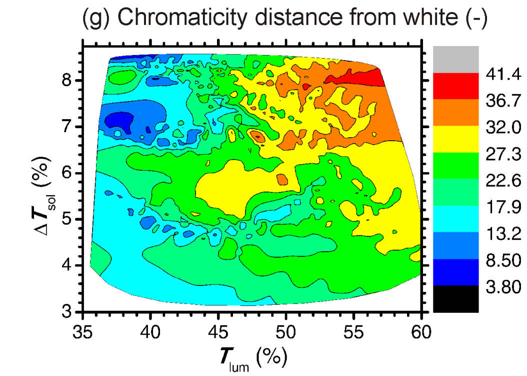
[J. Houska, Sol. Energy Mater. Sol. Cells 230, 111210 (2021)]

High T_{lum} & ΔT_{sol} at $h_{b,t} \approx 180$ nm
2nd-order maxima of $T(\lambda)$ in the visible ⇒
1st-order maxima of $T(\lambda)$ in the infrared

White chromaticity at $h_{b,t} \approx 130$ nm
at a cost of minimum $T(\lambda)$ in the visible



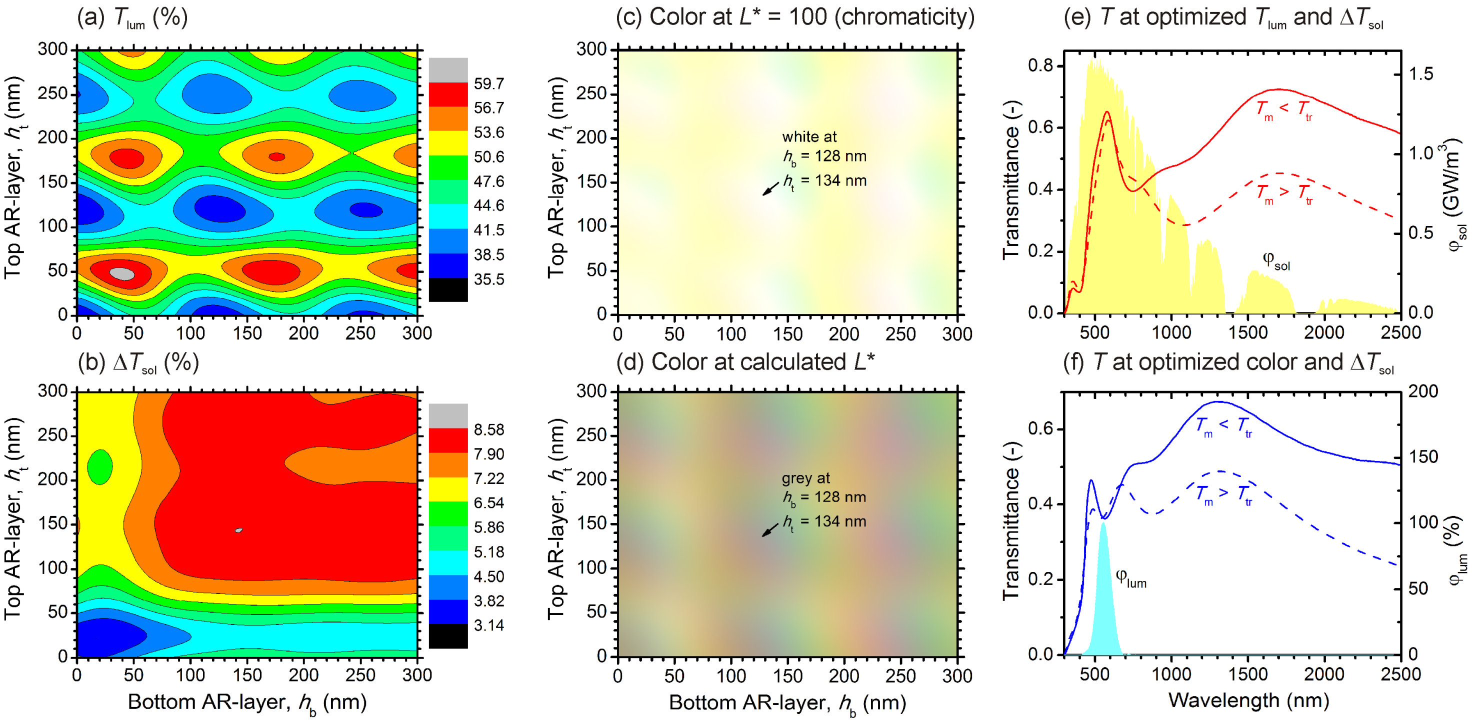


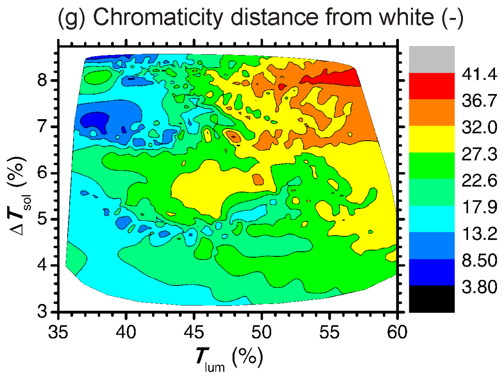
shown for
ZrO$_2$ (h_t)
V$_{1-x}$W$_x$O$_2$ (h)
ZrO$_2$ (h_b)

h = 50 nm
if not stated
otherwise

[J. Houska, Sol. Energy Mater. Sol. Cells 230, 111210 (2021)]

Chromaticity distance from white, $\sqrt{(a^{*2}+b^{*2})}$ in L*a*b* space, independent of T_{lum} & ΔT_{sol}
⇒ complicated space of properties.





shown for
ZrO_2 (h_t)
$V_{1-x}W_xO_2$ (h)
ZrO_2 (h_b)

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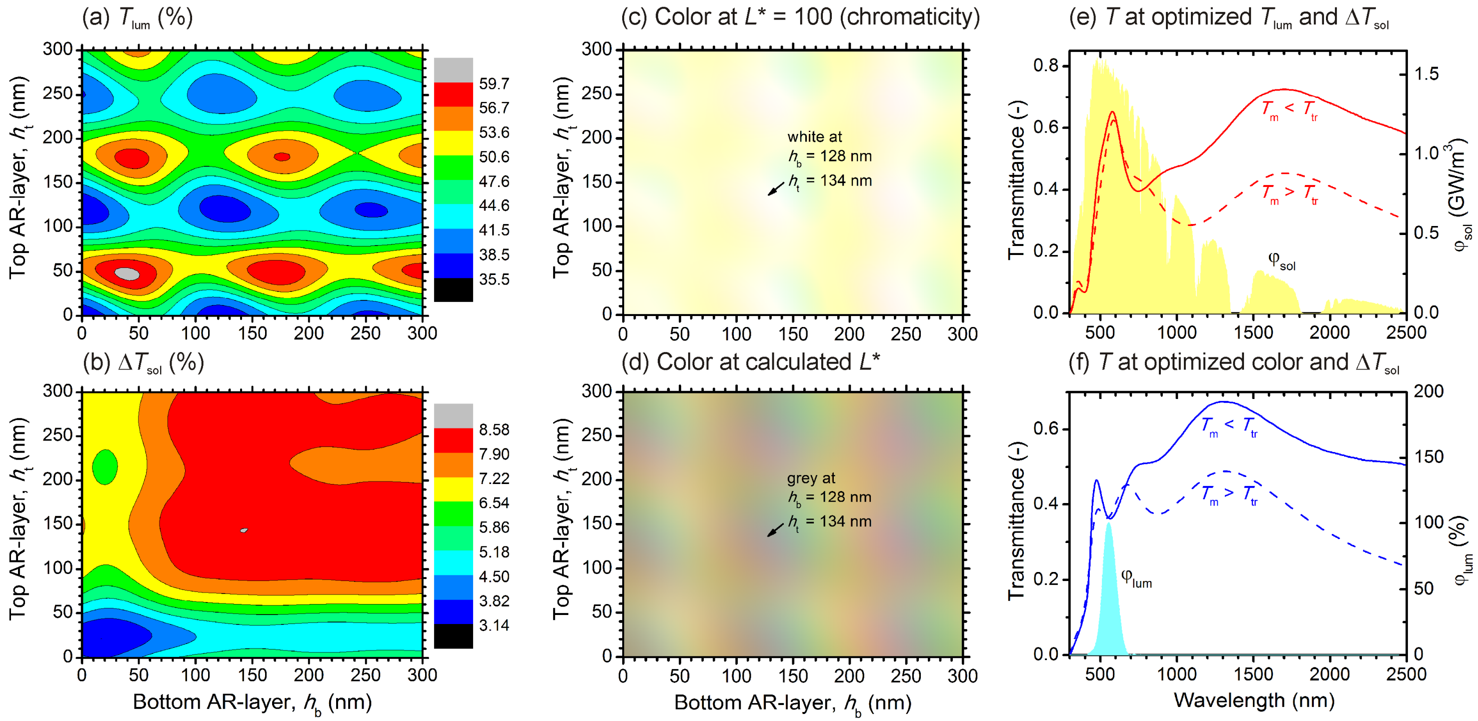
[J. Houska, Sol. Energy Mater. Sol. Cells 230, 111210 (2021)]

Chromaticity distance from white, $\sqrt{(a^{*2}+b^{*2})}$ in L*a*b* space, independent of T_{lum} & ΔT_{sol}
⇒ complicated space of properties.

At gived thickness of $V_{1-x}W_xO_2$
- tradeoff between T_{lum} and color



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ZrO_2 (h_b)

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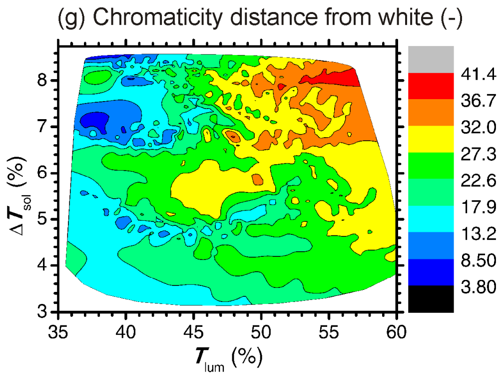
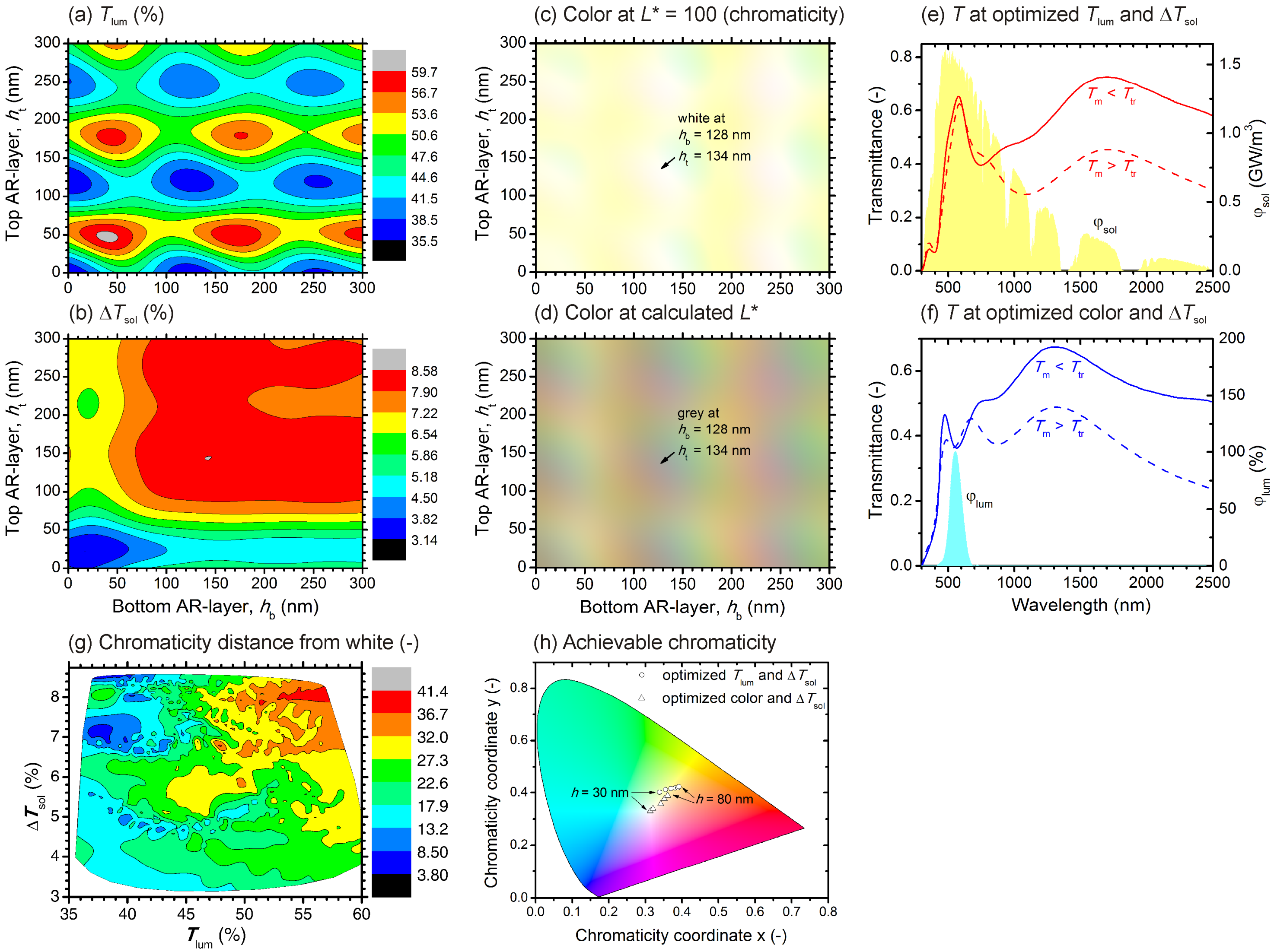
[J. Houska, Sol. Energy Mater. Sol. Cells 230, 111210 (2021)]



Chromaticity distance from white, $\sqrt{(a^{*2}+b^{*2})}$ in L*a*b* space, independent of T_{lum} & ΔT_{sol} ⇒ complicated space of properties.

At gived thickness of $V_{1-x}W_xO_2$
- tradeoff between T_{lum} and color
- no tradeoff between ΔT_{sol} and color



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ZrO_2 (h_b)

h = 50 nm
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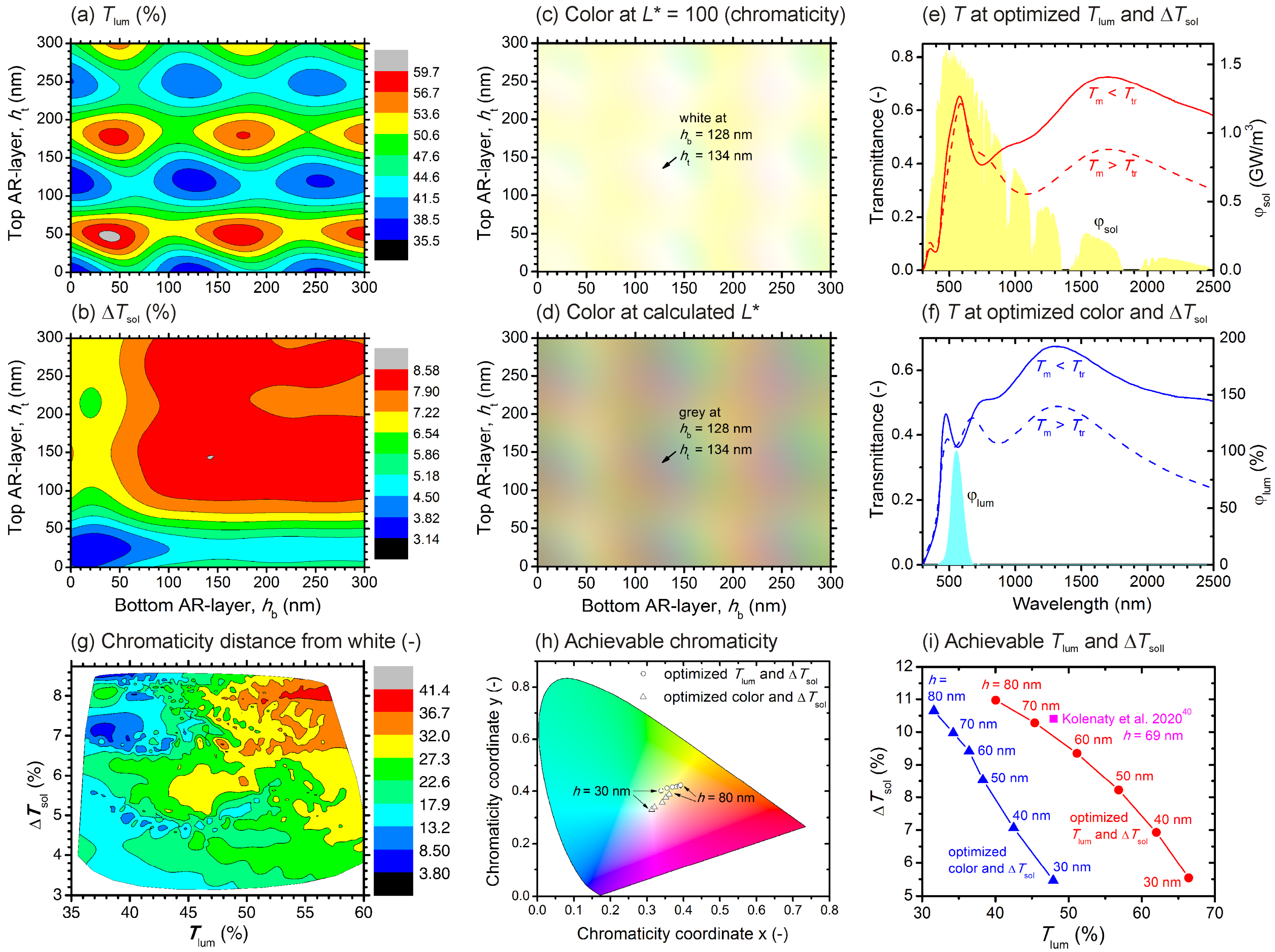
otherwise

[J. Houska, Sol. Energy Mater. Sol. Cells 230, 111210 (2021)]

In parallel, the coating color depends on $V_{1-x}W_xO_2$ thickness

- at optimized T_{lum}
- at optimized color



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ZrO_2 (h_t)
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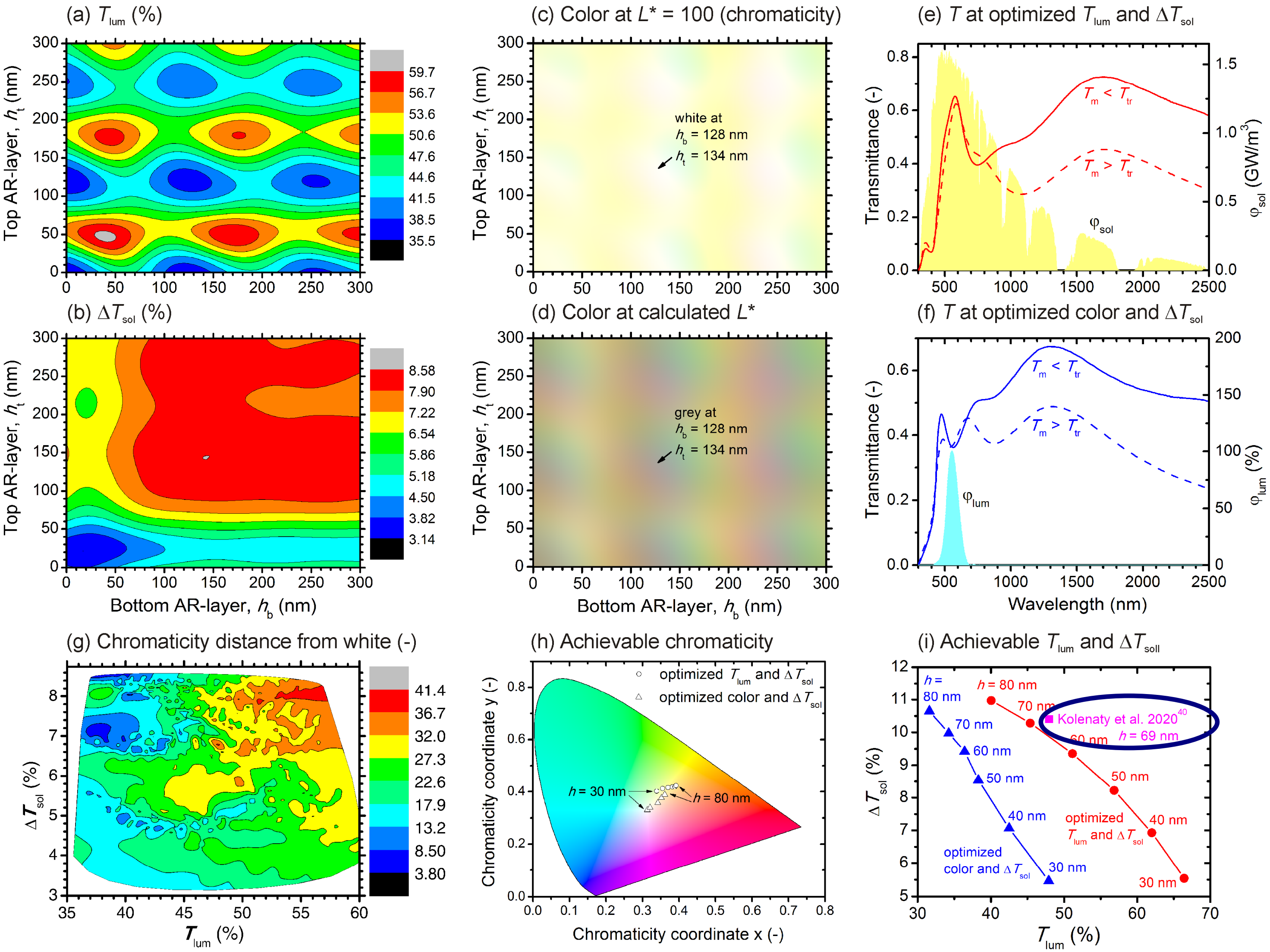
ZrO_2 (h_b)

h = 50 nm
if not stated
otherwise

[J. Houska, Sol. Energy Mater. Sol. Cells 230, 111210 (2021)]

- Tradeoff between T_{lum} and ΔT_{sol}: role of $V_{1-x}W_xO_2$ thickness at optimized T_{lum} as well as at optimized color



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[J. Houska, Sol. Energy Mater. Sol. Cells 230, 111210 (2021)]

- Tradeoff between T_{lum} and ΔT_{sol}: role of $V_{1-x}W_xO_2$ thickness at optimized T_{lum} as well as at optimized color
- Agreement with an example of experimental result

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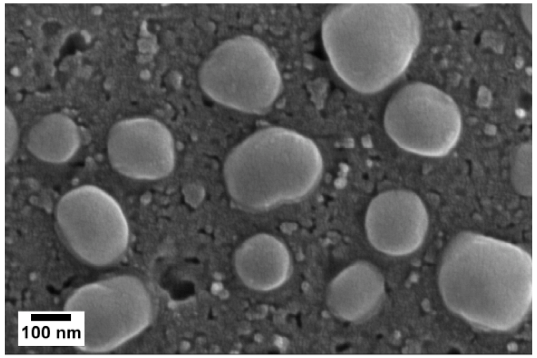
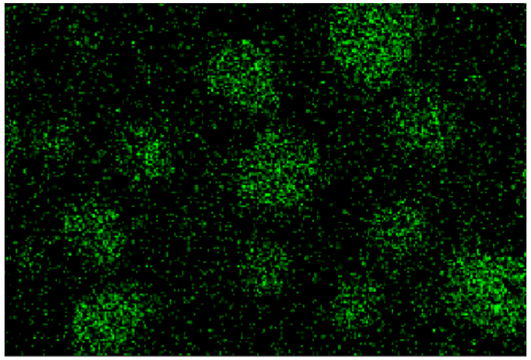
VO_2(-based) nanoparticles in dielectric matrix

(a) SEM of sputtered[54,102] VO_2-SiO_2

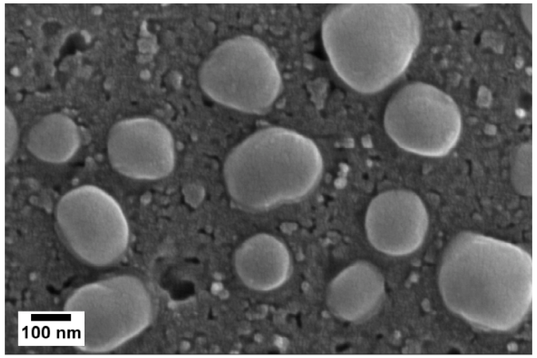


(b) EDX of sputtered[54,102] VO_2-SiO_2 (green V)



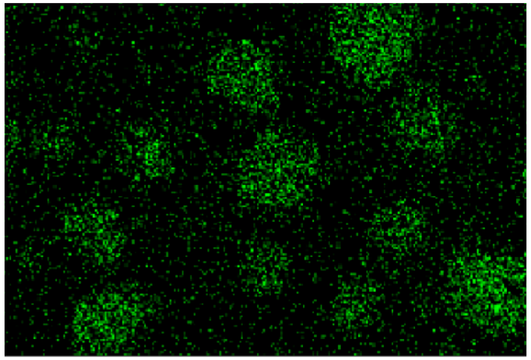
[C.G. Granqvist and G.A. Niklasson, Buildings 7, 3 (2017)]

(a) SEM of sputtered[54,102] VO_2-SiO_2



[C.G. Granqvist and G.A. Niklasson, Buildings 7, 3 (2017)]

(b) EDX of sputtered[54,102] VO_2-SiO_2 (green V)

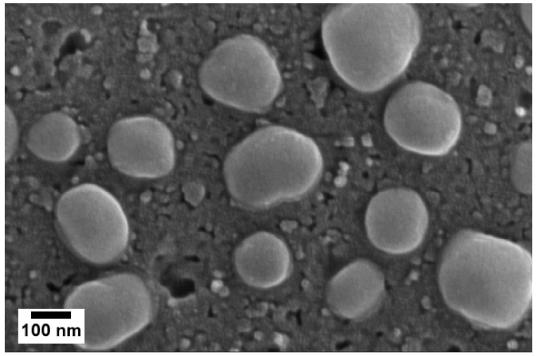


VO_2(-based) nanoparticles in dielectric matrix

$\Downarrow$

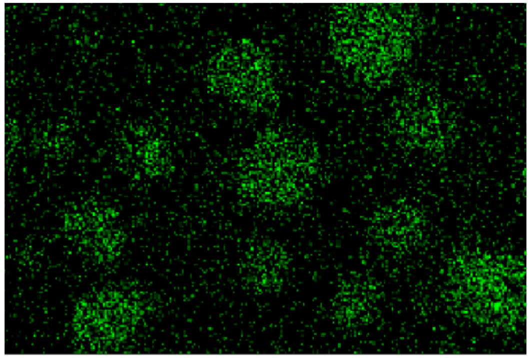
metal / dielectric interface above T_{tr} (VO_2 is metallic)

(a) SEM of sputtered[54,102] VO_2-SiO_2

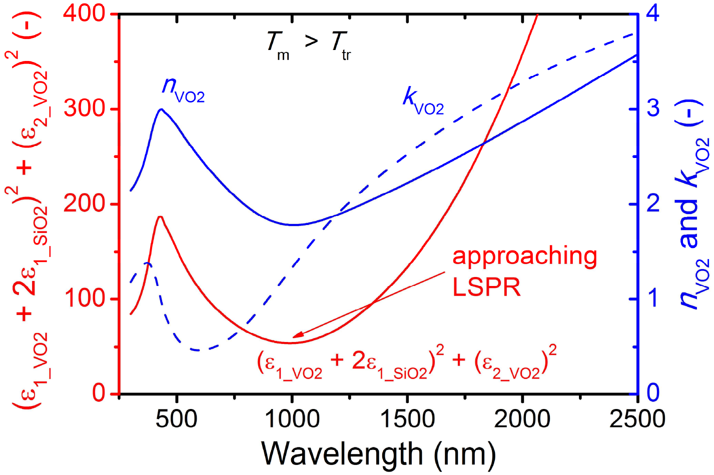


[C.G. Granqvist and G.A. Niklasson, Buildings 7, 3 (2017)]

(b) EDX of sputtered[54,102] VO_2-SiO_2 (green V)



(d) Optical properties of sputtered[39] $V_{1-x}W_xO_2$



[calculation using the same properties of our VO_2 as above]

VO_2(-based) nanoparticles in dielectric matrix

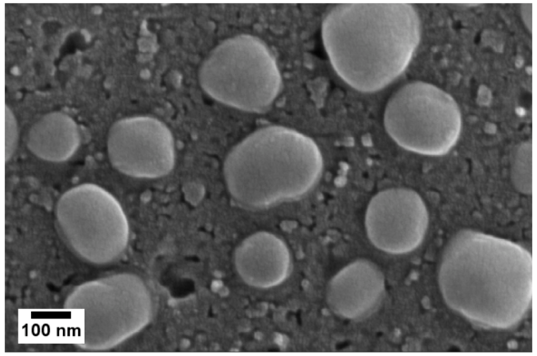
⇓

metal / dielectric interface above T_{tr} (VO_2 is metallic)

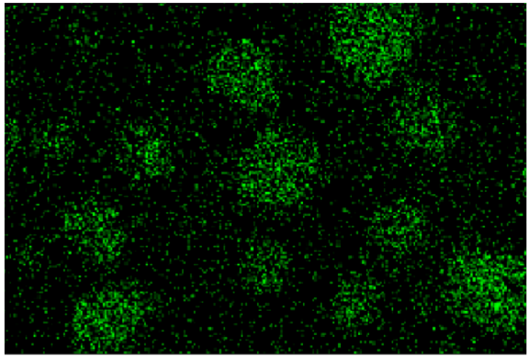
⇓

approaching localized surface plasmon resonance in the near infrared above T_{tr}

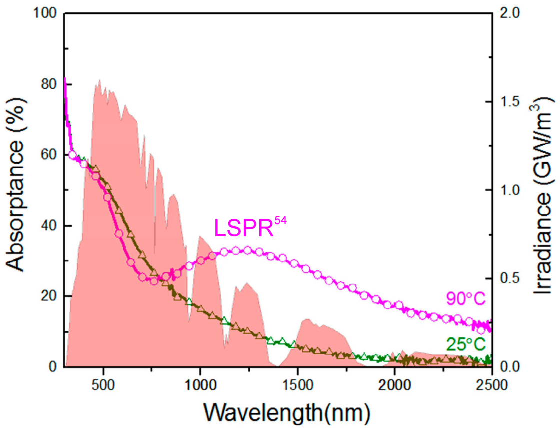
(a) SEM of sputtered[54,102] VO_2-SiO_2



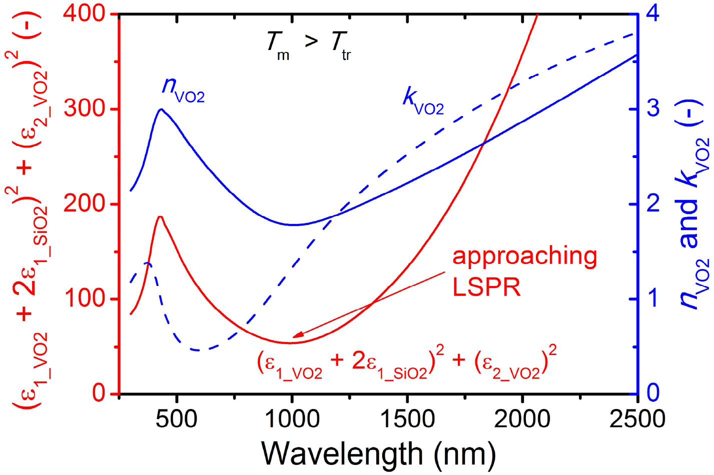
(b) EDX of sputtered[54,102] VO_2-SiO_2 (green V)



(c) Absorption in sputtered[54,102] VO_2-SiO_2



(d) Optical properties of sputtered[39] $V_{1-x}W_xO_2$



[C.G. Granqvist and G.A. Niklasson, Buildings 7, 3 (2017)]

[calculation using the same properties of our VO_2 as above]

VO_2(-based) nanoparticles in dielectric matrix

⇓

metal / dielectric interface above T_{tr} (VO_2 is metallic)

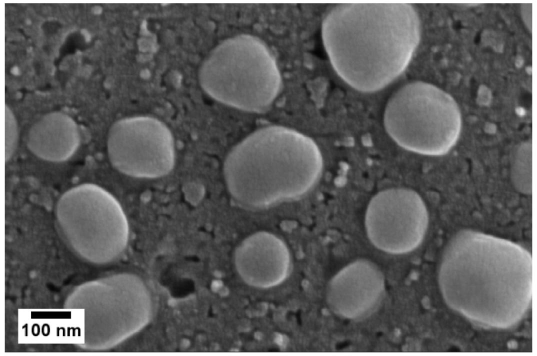
⇓

approaching localized surface plasmon resonance in the near infrared above T_{tr}

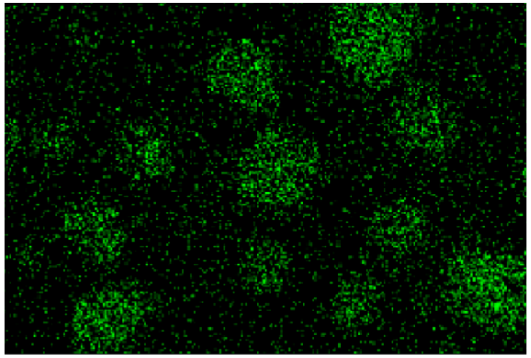
⇓

enhanced $A(\lambda)$ in the near infrared above T_{tr}

(a) SEM of sputtered[54,102] VO_2-SiO_2



(b) EDX of sputtered[54,102] VO_2-SiO_2 (green V)



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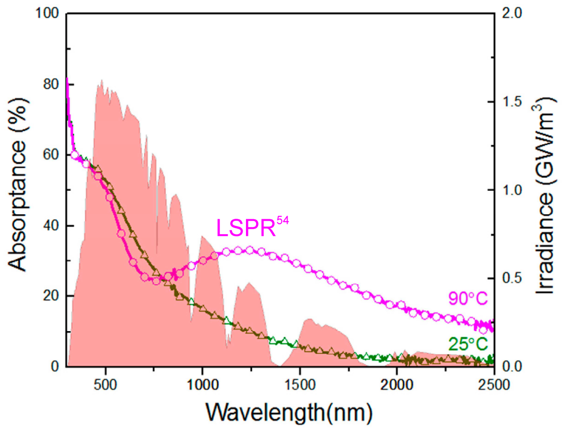

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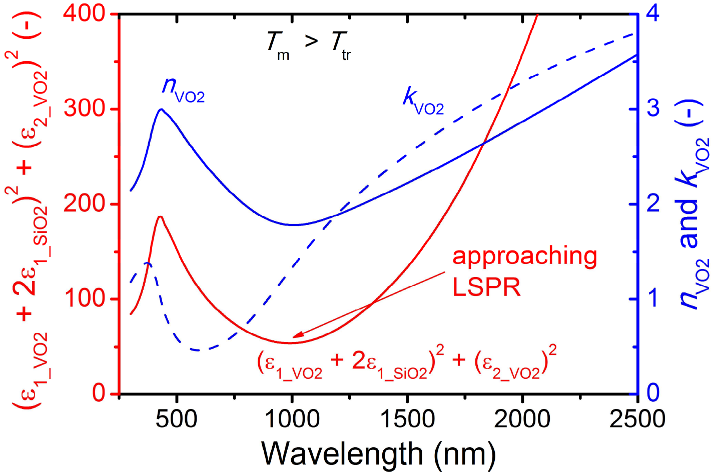

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⇓

enhanced $A(\lambda)$ in the near infrared above T_{tr}

⇐

Enhanced modulation of $T(\lambda)$ in the near infrared, enhanced ΔT_{sol}

Outline

I. Introduction and background

II. Quantities of interest and criteria of success

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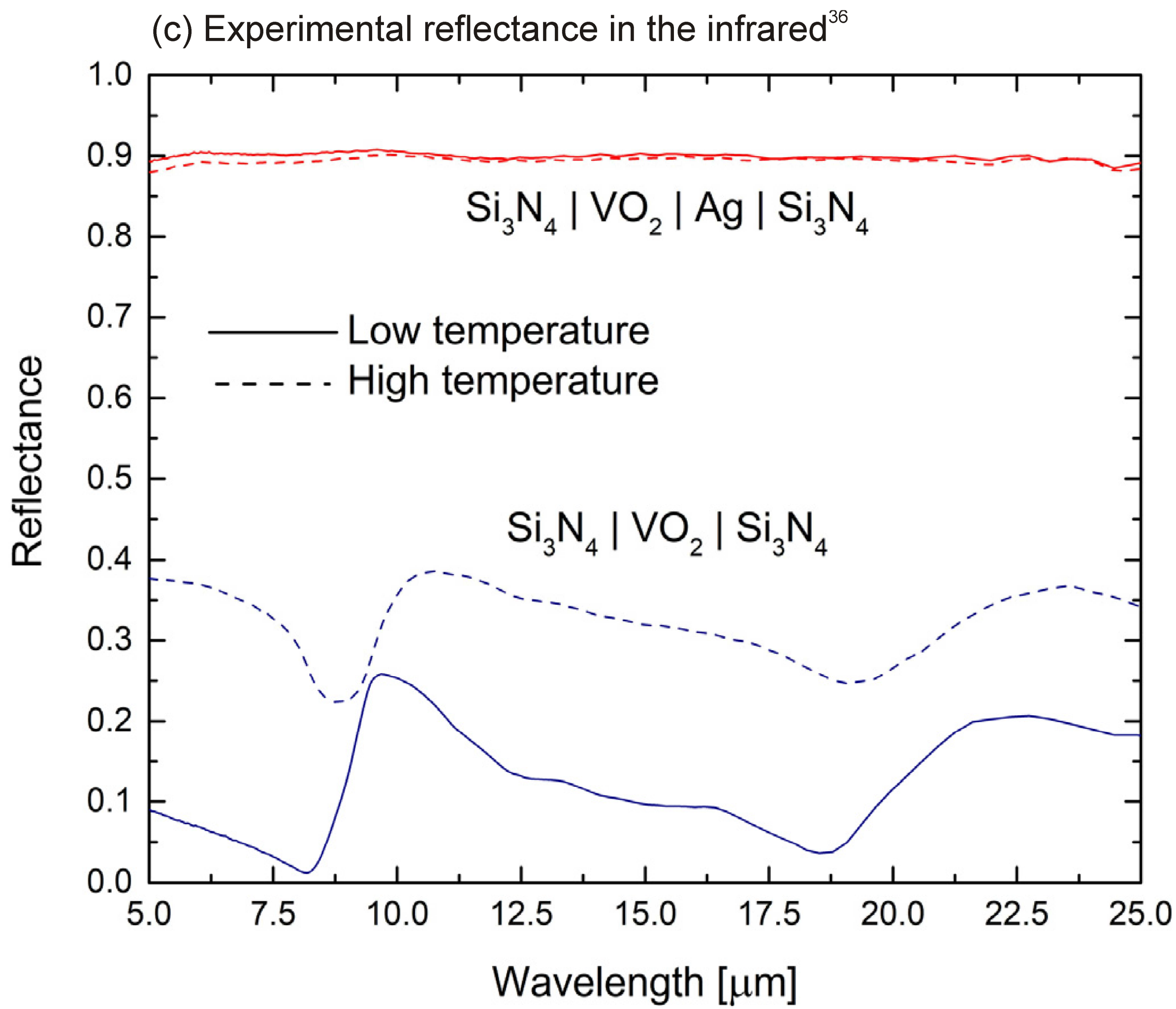
IV. Ways to improve the coating characteristics

- A. Suitable doping elements
- B. Suitable materials of antireflection layers
- C. Design of multilayers with optimized ΔT_{sol} and T_{lum}
- D. Design of multilayers with optimized ΔT_{sol} and color
- E. Designs based on layers containing VO_2 nanoparticles
- **F. Decreasing the coating emissivity in the infrared**

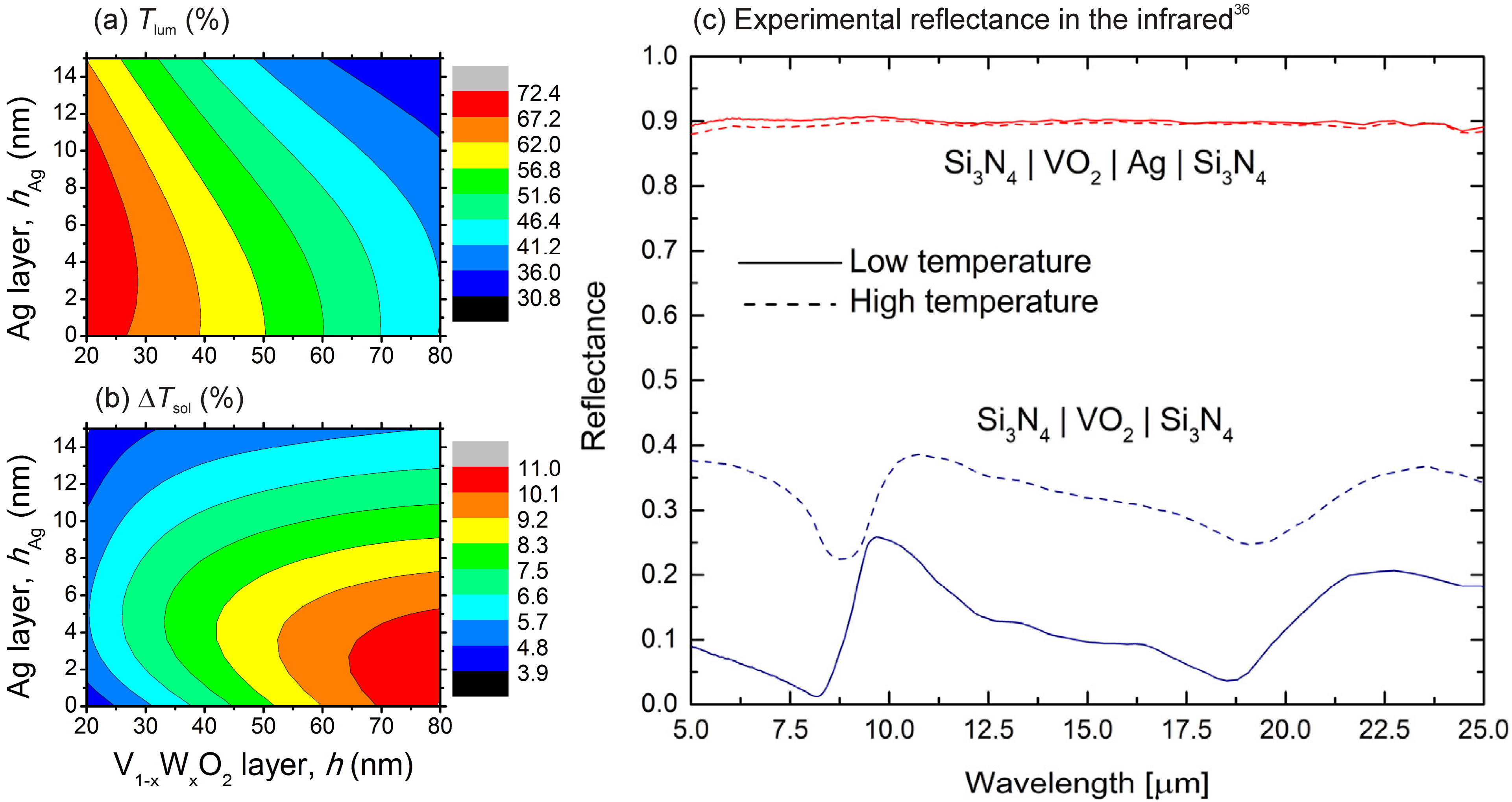
V. Sputtering of high-performance VO_2-based multilayers

VI. Summary and outlook



[B. Baloukas, S. Loquai, and L. Martinu, Sol. Energy Mater. Sol. Cells 183, 25 (2018)]

Thin Ag layers (low-emissivity glass, in itself widely used) can be combined with VO_2-based thermochomic layers



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Few nm Ag: only slightly lower T_{lum}, even slightly higher ΔT_{sol}

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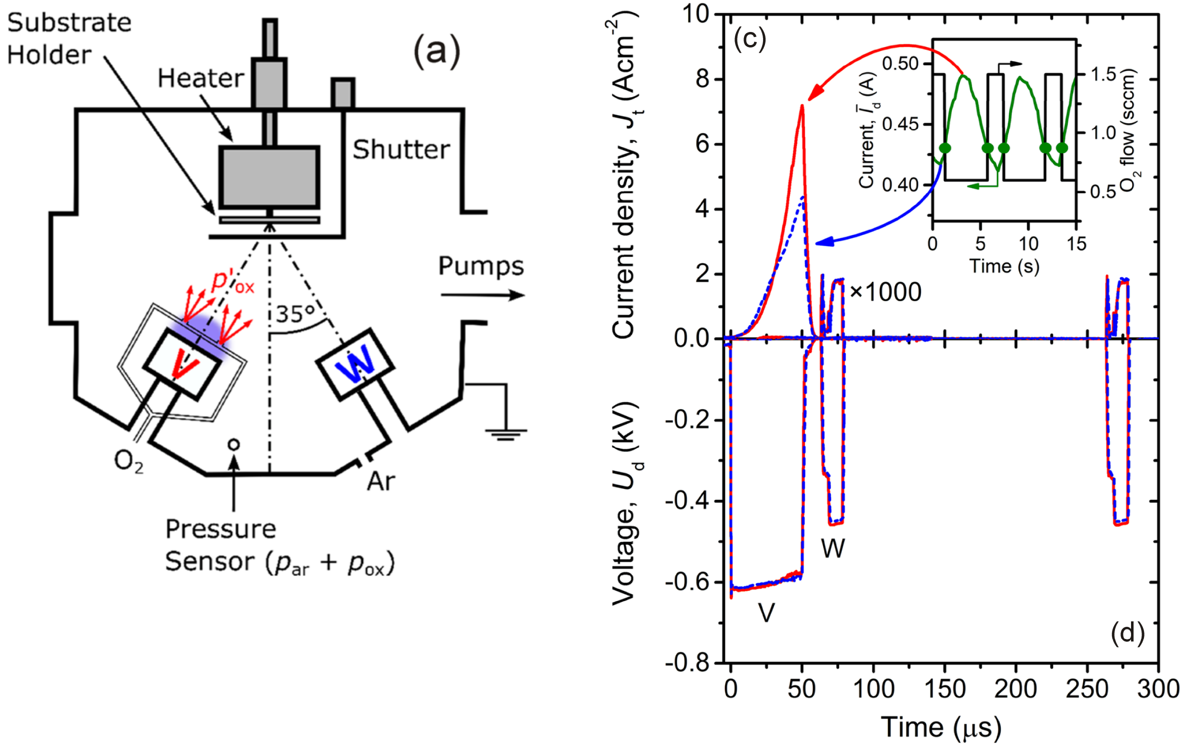
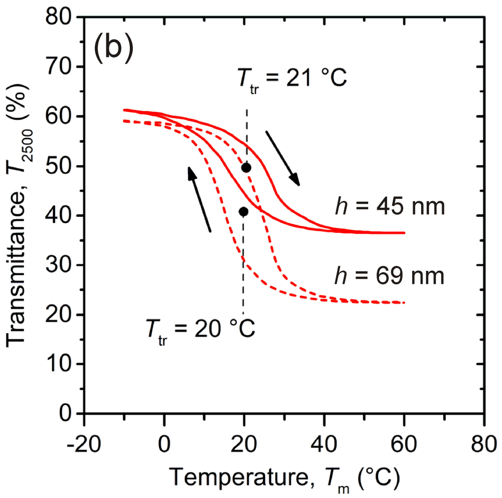
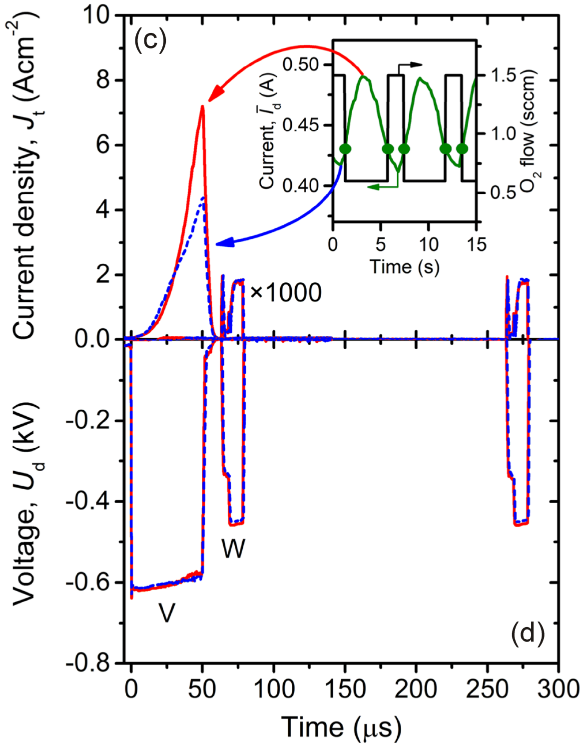


HiPIMS of V
(13 Wcm^{-2}, 200 Hz,
t_{on} = 50µs, 1% duty c.)

complemented by

pulsed dc sput. of W
(33 mWcm^{-2}, 5 kHz,
t_{on} = 16µs, 8% duty c.)





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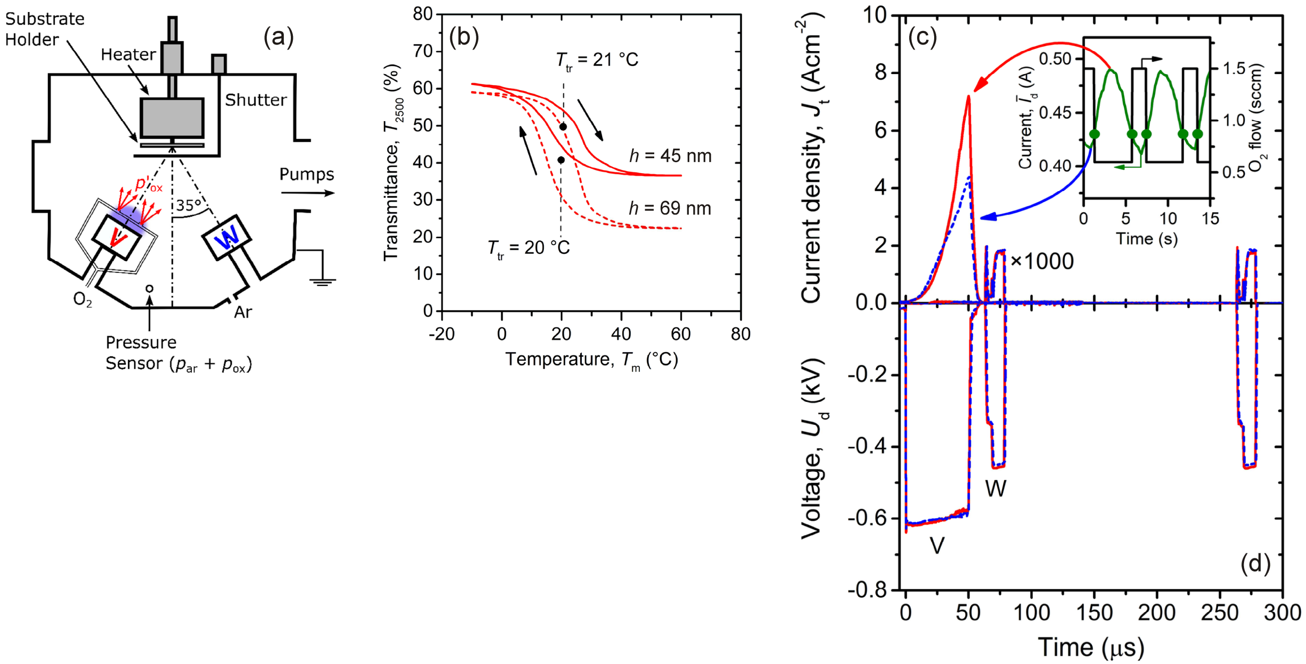
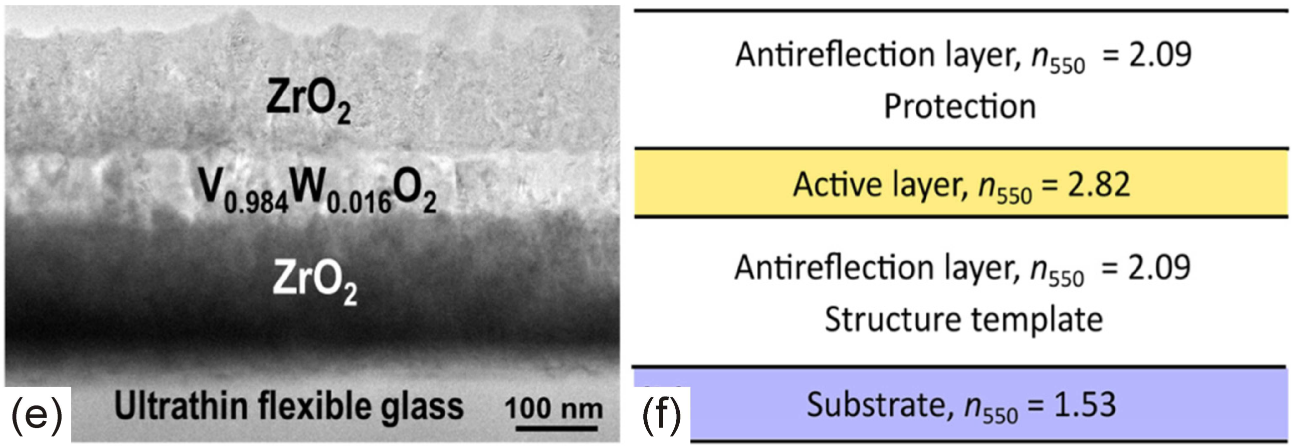
1.6-1.8 at.% W in
the V sublattice
⇓
T_{tr} lowered to 20 °C at
preserved T_{lum} & ΔT_{sol}



$ZrO_2/V_{1-x}W_xO_2/ZrO_2$ (2^{nd}-order AR-layers)

⇓

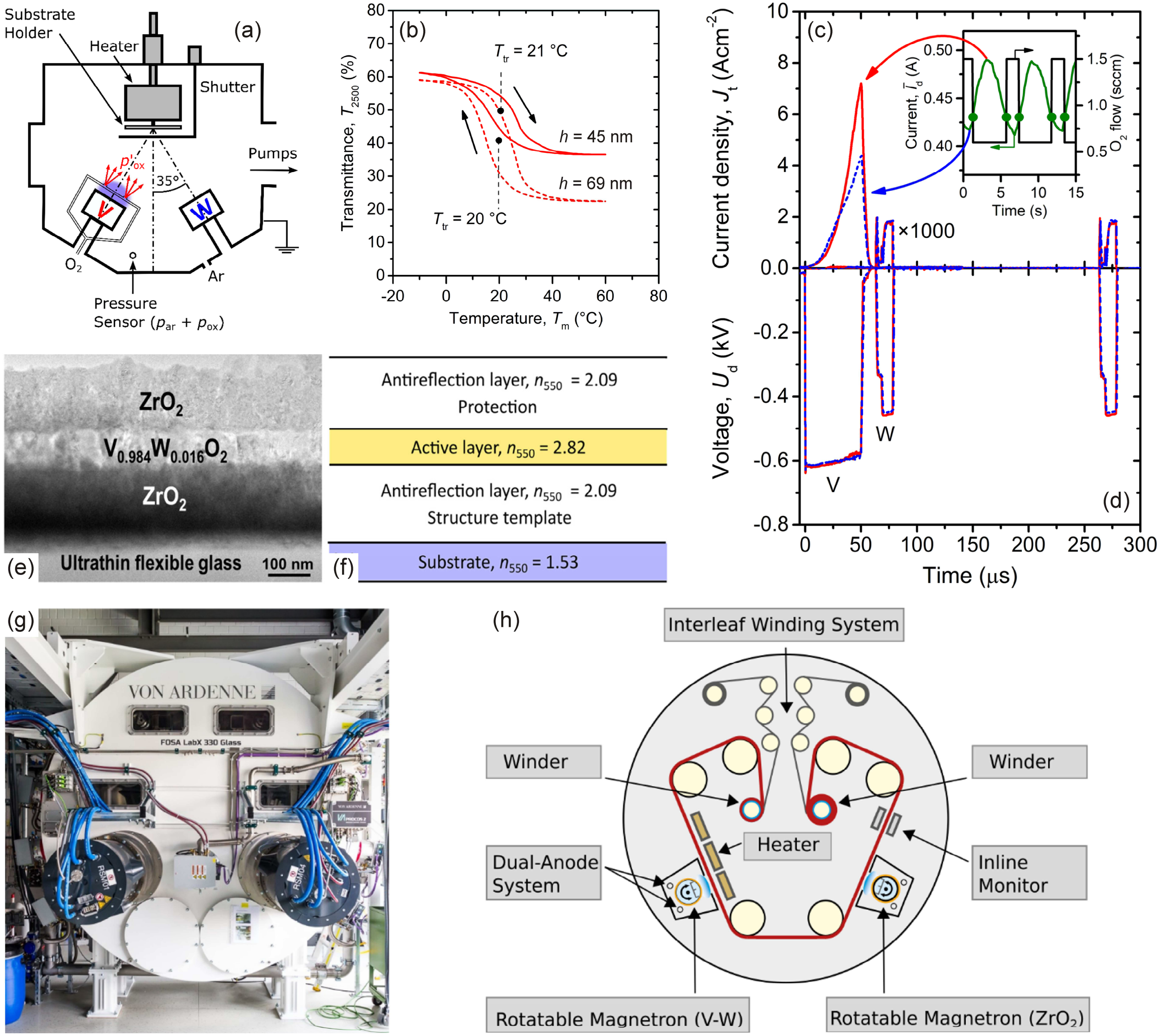
T_{lum} ≈50%,
ΔT_{sol} ≈10%
T_{tr} ≈20°C
T_s ≈330°C



realized on ultrathin flexible glass in

- laboratory-scale device: UWB Plzen

[D. Kolenaty et al., Sci. Rep. 10, 11107 (2020)]
[T. Barta et al., Coatings 10, 1258 (2020)]



[J. Rezek et al., Surf. Coat. Technol., in print (2022)]

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realized on ultrathin flexible glass in

- laboratory-scale device: UWB Plzen
- large roll-to-roll device (30 cm × 20 m): collaborat. with FEP Dresden

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Summary and outlook *[J. Houska, J. Appl. Phys. 131, 110901 (2022)]*

Reactively sputtered VO_2-based thermochromic coatings

- very interesting from the perspective of fundamental research
- competitive performance (**UWB:** T_{lum}≈50%, ΔT_{sol}≈10%, T_{tr}≈20°C, T_s≈330°C)
- can be prepared under industry-friendly conditions
- show an enormous potential for near future applications

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The following is recommended to be kept in mind

- all main quantities should be optimized in parallel (energy saving windows: T_{lum}, ΔT_{sol}, T_{tr}, T_s)
- increasing importance of color, shape of hysteresis loop, environmental stability, emissivity, realistic beam angles, absorption in realistic substrates
- each improvement should be explained: distinguish reproducible benefits of an innovative coating design from e.g. slight compositional changes.

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Main ideas how to improve the coating properties

- energetic bombardment using controlled reactive HiPIMS
- doping (W, Mg, ...) using techniques which do not harm other properties
- $T(\lambda)$ modulation in the visible by slight changes of [V]/[O] ratio
- second order antireflection layers
- localized surface plasmon resonance