Design of high-performance VO_2-based thermochromic coatings, and pathway for their low-*T* preparation

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DEPARTMENT OF PHYSICS

NTIS

Acknowledgment

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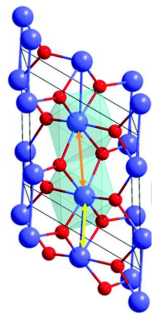
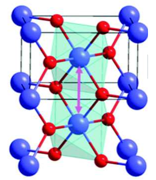
Thermochromic VO_2

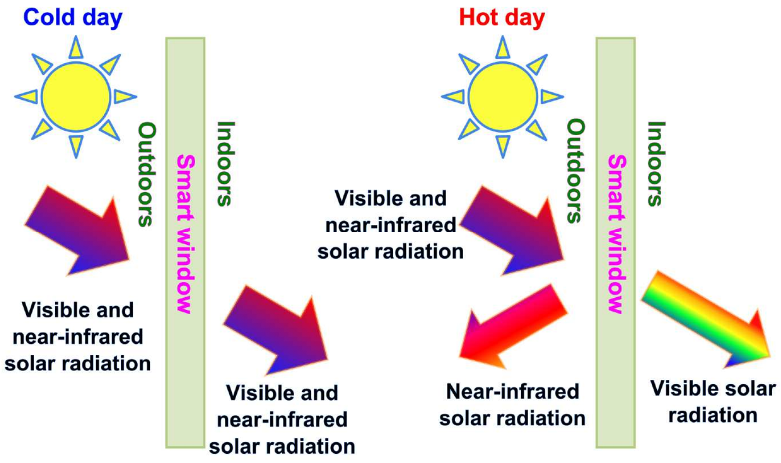


Low temperature (monoclinic):
- semiconductor (band gap)
- transparent
- low eletrical and thermal conductivity



High temperature (tetragonal rutile):
- metallic
- opaque in IR
- high electrical and thermal conductivity

Applications
- smart energy-efficient windows (!)
- optical switches
- smart radiators
- protection of IR detectors
- thermal management in cars, ...



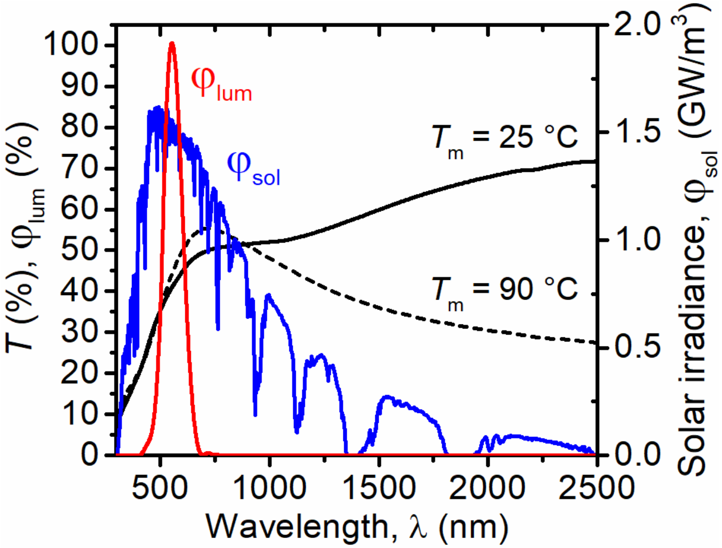
Challenges

Prepare VO_2 films by industry-friendly technique

- low temperature (≤300°C or so)
- technique allowing easy upscaling
- no substrate bias voltage (rf, or dc + conductive interlayer)

Achieve superior optical properties

- thermochromic transition temperature close to RT
- high luminous transmittance, T_{lum}
- high modulation of solar transmittance, ΔT_{sol}



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

$$T_{sol} = \int_{300}^{2500} \varphi_{sol}(\lambda)T(\lambda,T_m)d\lambda \Big/ \int_{300}^{2500} \varphi_{sol}(\lambda)d\lambda$$

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How to prepare VO_2 on amorphous unbiased glass at 300°C

J. Vlcek et al., J. Phys. D Appl. Phys. 50, 38LT01 (2017)
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What is the optimum design of VO_2-based multilayers

(parallel optimization of T_{lum} and ΔT_{sol})

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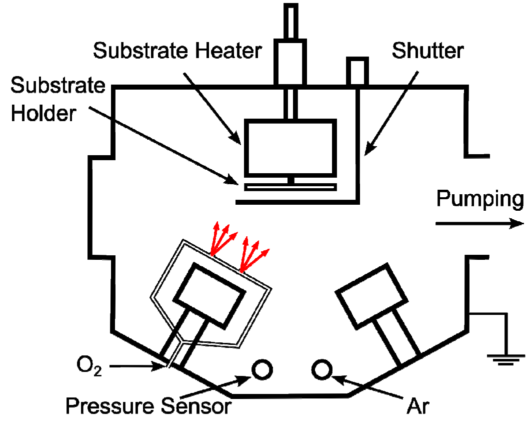
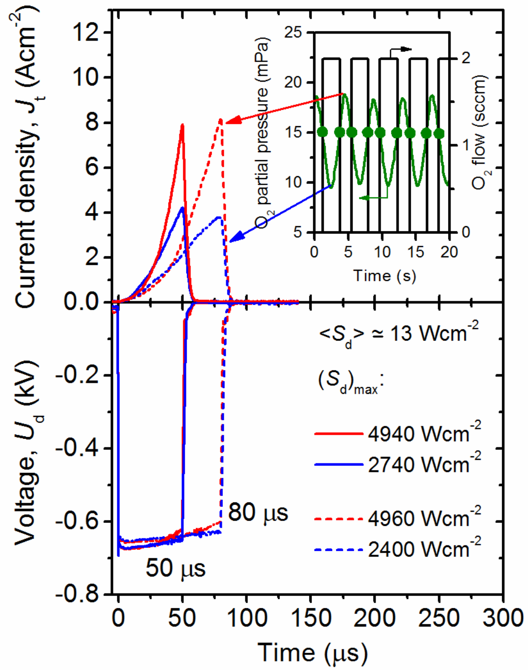
Deposition technique

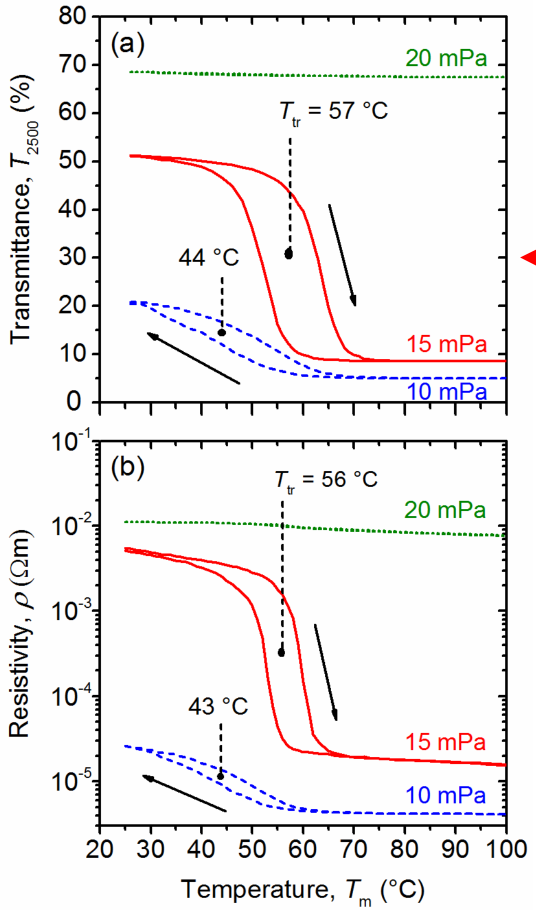
High power impulse magnetron sputtering of V in Ar+O_2 plasma
⇓
highly ionized fluxes with many metal ions
⇓
crystallinity & densification without bias at
250 °C on crystalline Si substrate
300 °C on amorphous glass substrate
(literature before 2016: ≥400 °C)

Pulsed reactive gas flow control
(European patent 2015)
⇓
exactly as much oxygen as we need
⇓
VO_2 film stoichiometry (×V_2O_5, ×V_2O_3)



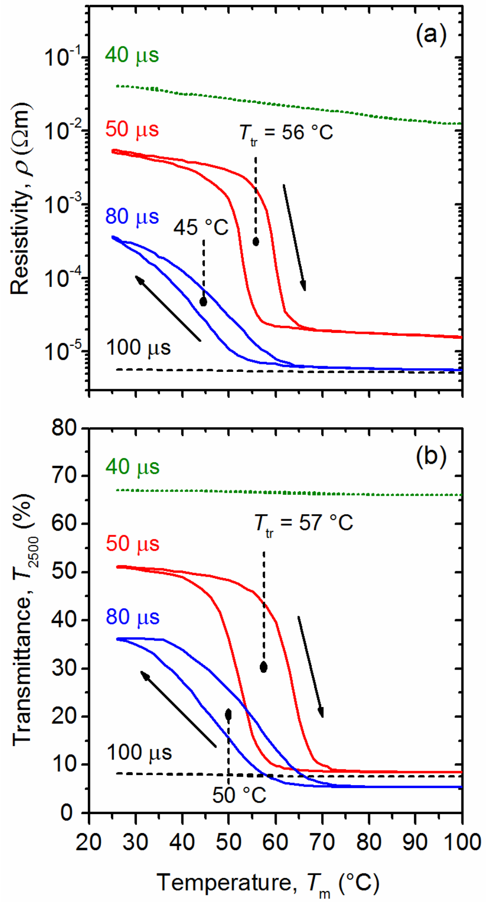


Narrow windows for critical process parameters



Narrow window (±10%) of critical O_2 pressures leading to crystalline thermochromic VO_2 (×V_2O_5, V_2O_3, etc.)

Cross-check by XRD and Raman (not shown)



O_2 window closes from ±10% to zero at improper voltage pulse duration

Shorter pulse ⇒ more oxygen & better crystallinity (role of compound fraction on sputter target and ion flux characteristics)

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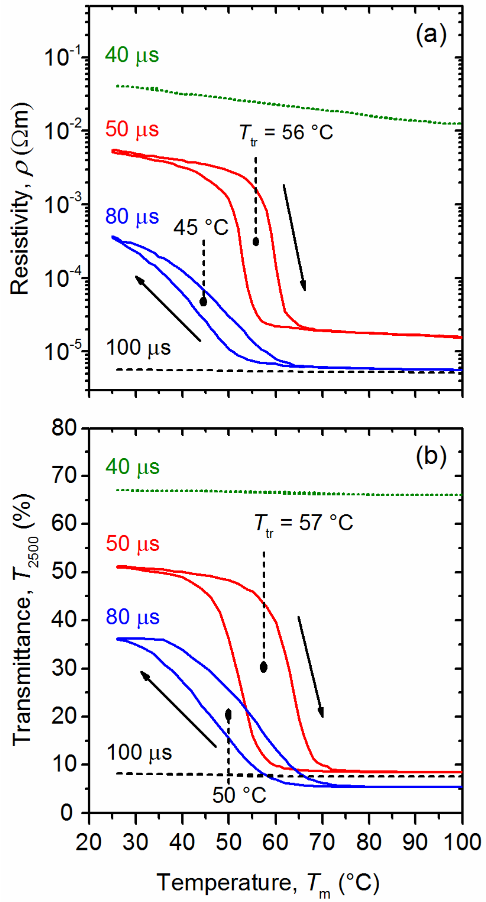
Shorter pulse ⇒ more oxygen & better crystallinity (role of compound fraction on sputter target and ion flux characteristics)

Crystalline substrate or interlayer: use pulse length leading to optimum composition (crystallinity ensured by epitaxial growth)

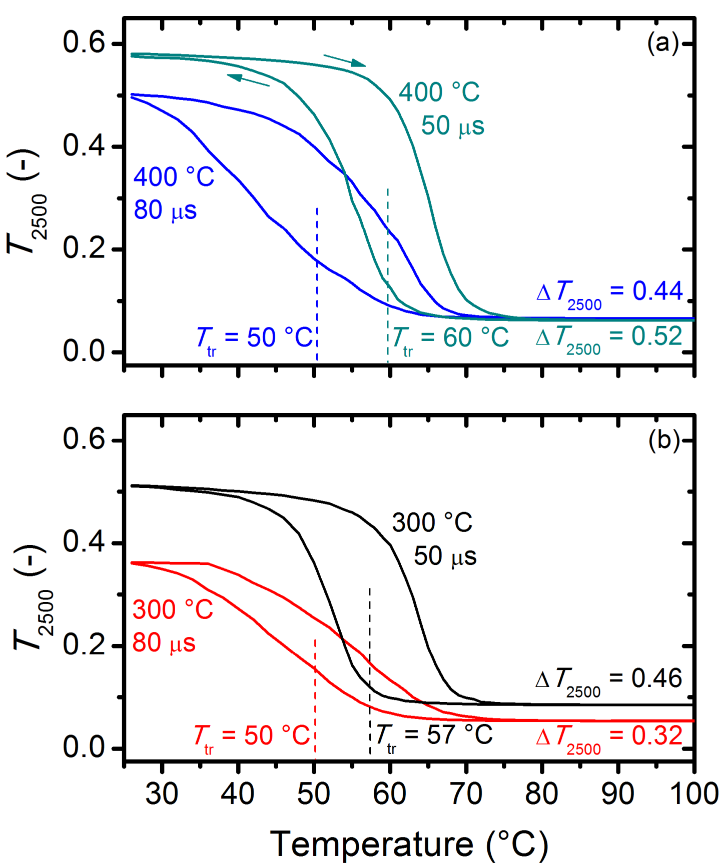
Amorphous substrate: must use sufficiently short pulse length leading to crystallinity (regardless slightly suboptimum composition)

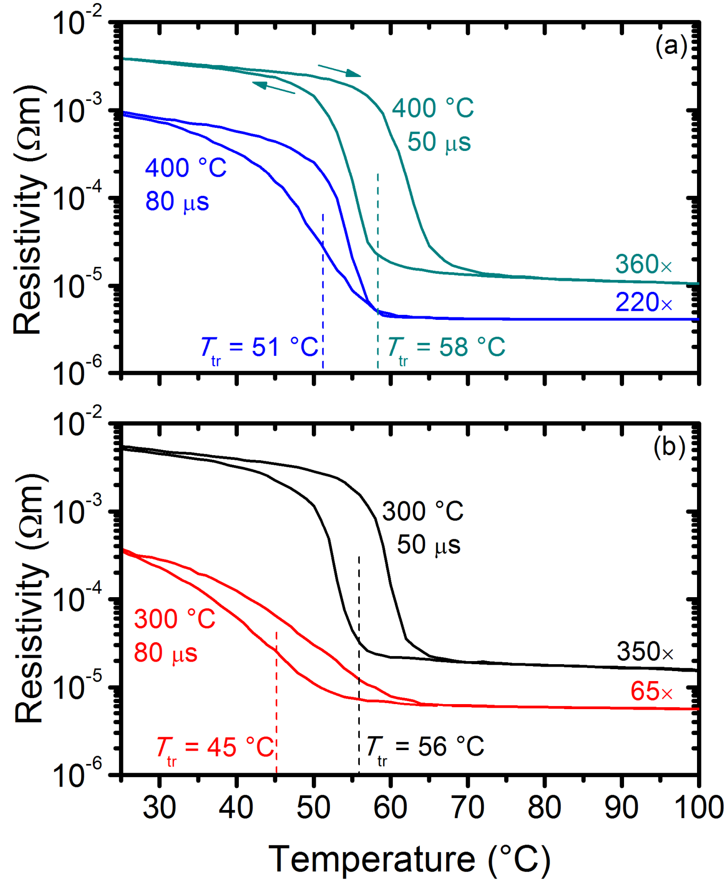


Properties of VO_2 prepared at 300°C on unbiased glass

Sufficiently short (50 μs) pulses ⇒ crystallinity due to ion bomb.
⇒ lowering *T* from 400 to 300°C does not harm the properties

Longer (80 μs) pulses ⇒ composition even closer to VO_2,
but worse crystallinity especially at 300 °C





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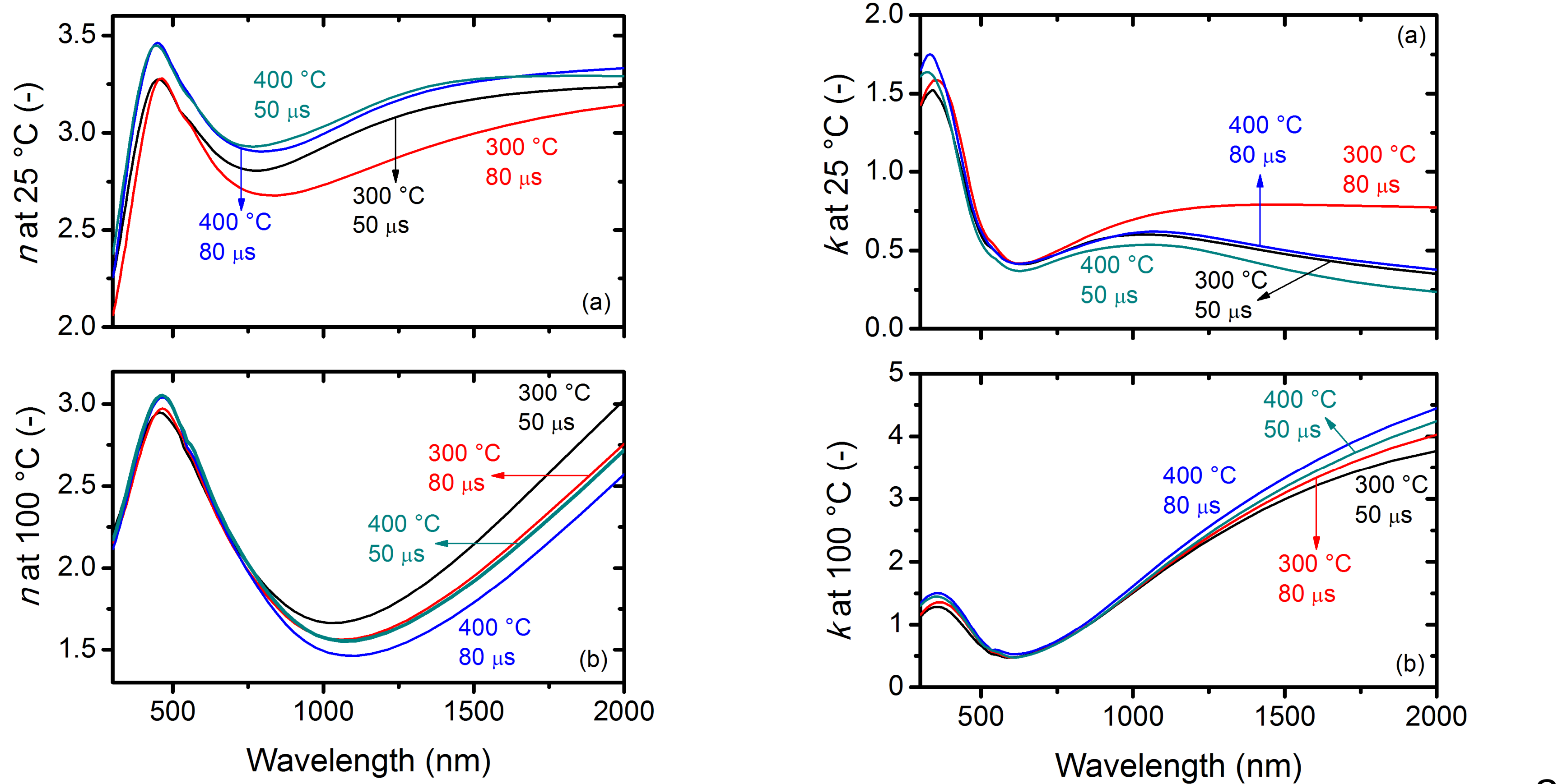

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How to maximize T_{lum} and ΔT_{sol}

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$$T_{sol} = \int_{300}^{2500} \varphi_{sol}(\lambda)T(\lambda,T_m)d\lambda \Big/ \int_{300}^{2500} \varphi_{sol}(\lambda)d\lambda$$

Varying VO_2 thickness $\Rightarrow$ tradeoff
(thin films have high T_{lum}, thick films have high ΔT_{sol})

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1st order antireflection layers ⇒ tradeoff
(first-order maximum of T_{lum} overlaps with minimum of ΔT_{sol})

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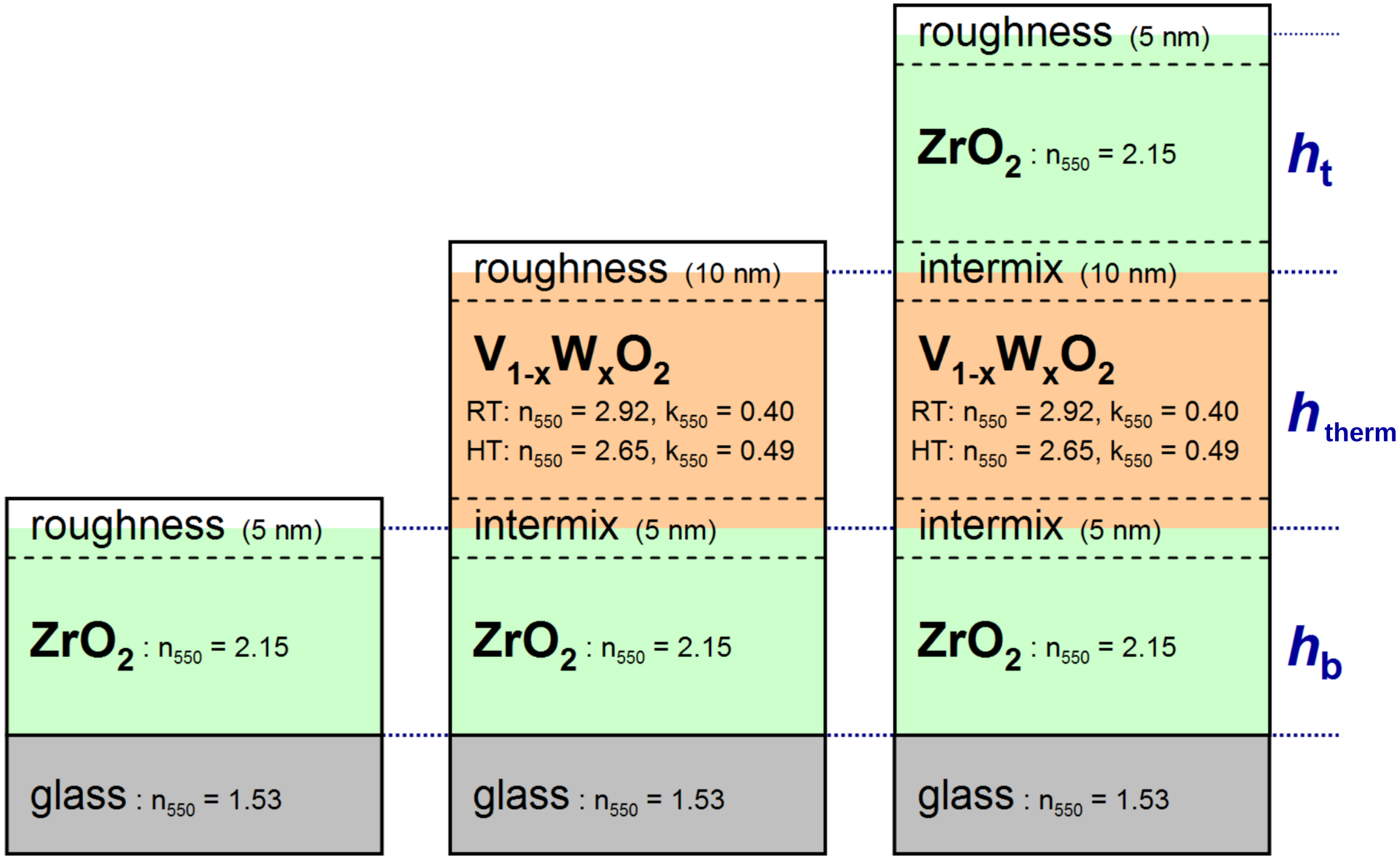
2nd order antireflection layers ⇒ improves both T_{lum} and ΔT_{sol}

How to maximize T_{lum} and ΔT_{sol}

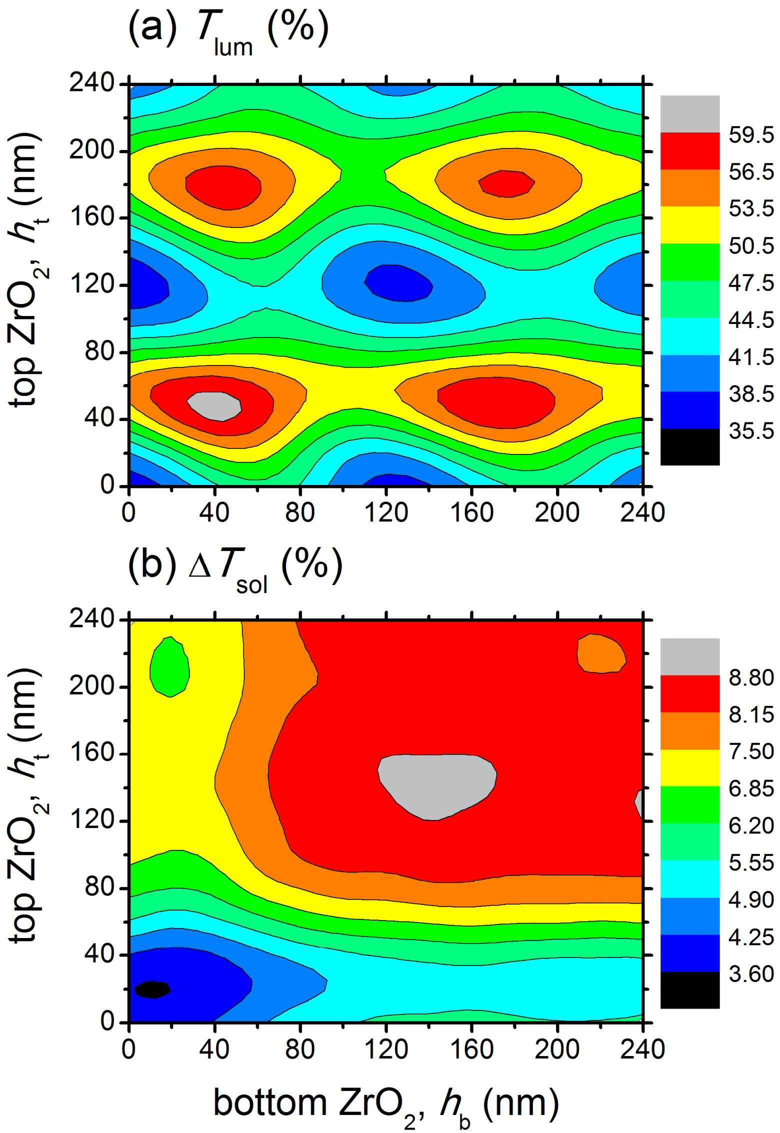
2nd order antireflection layers $\Rightarrow$ improves both T_{lum} and ΔT_{sol}

chosen material of antireflection layers: ZrO_2
chosen VO_2 or $V_{1-x}W_xO_2$ thickness in calculations below: 50 nm



How to maximize T_{lum} and ΔT_{sol} (at h_{therm} = 50 nm)

2nd order antireflection layers ⇒ improves both T_{lum} and ΔT_{sol}



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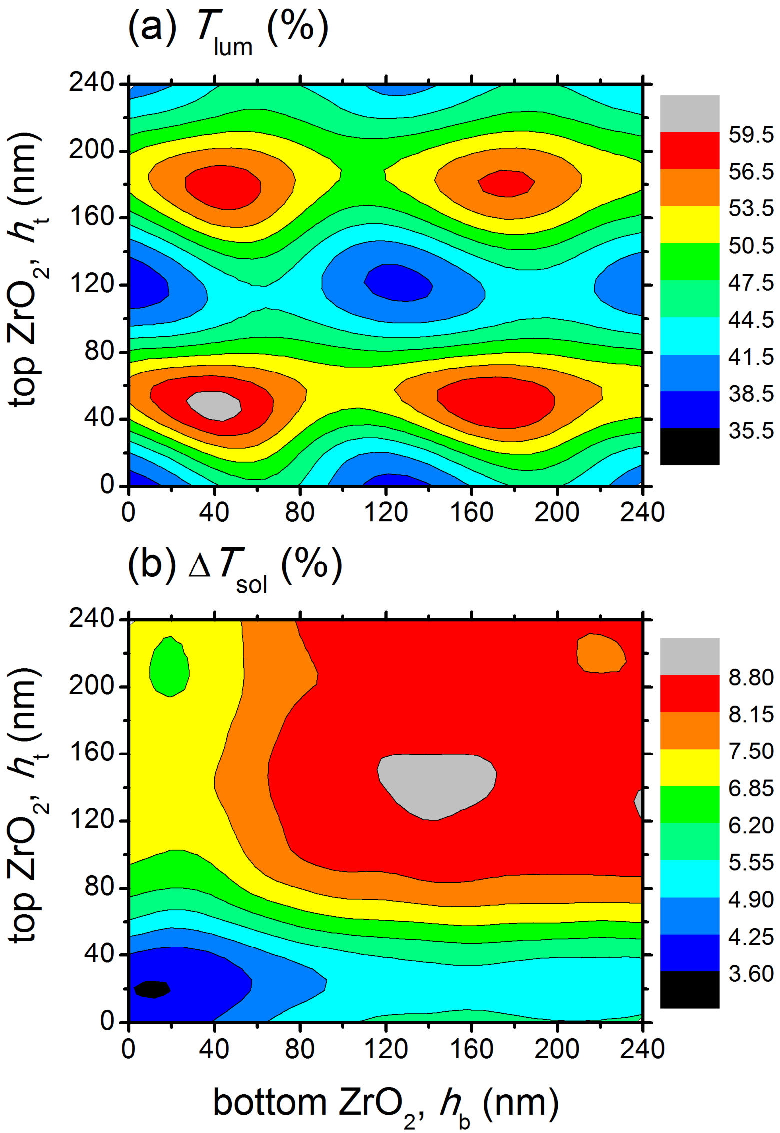


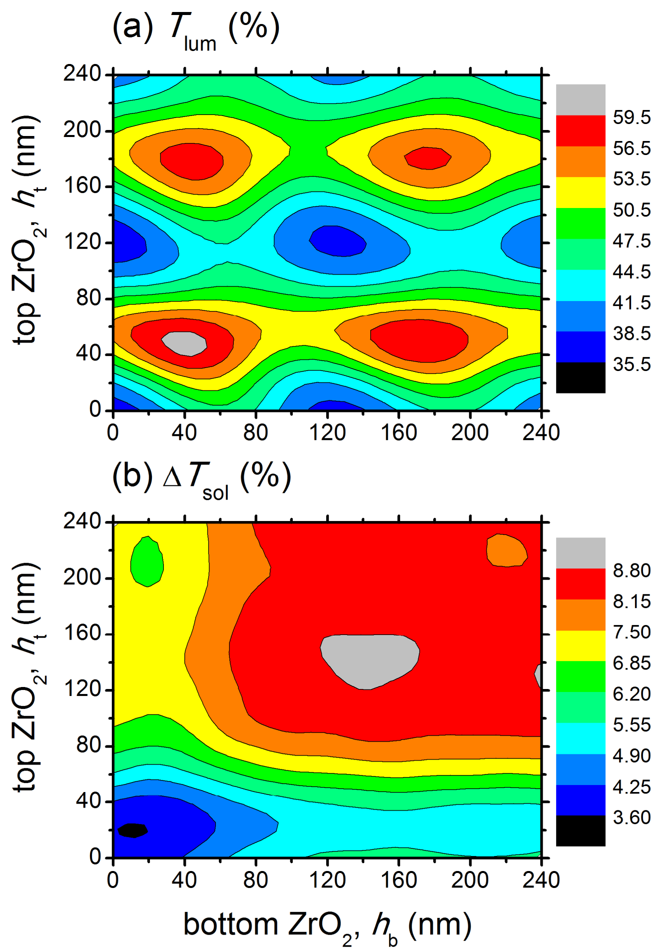
Peafowl-like figure for **T_{lum}:**

1st order maximum of T_{lum} (ZrO_2 thickness of ≈40 nm) corresponds to **low ΔT_{sol}**

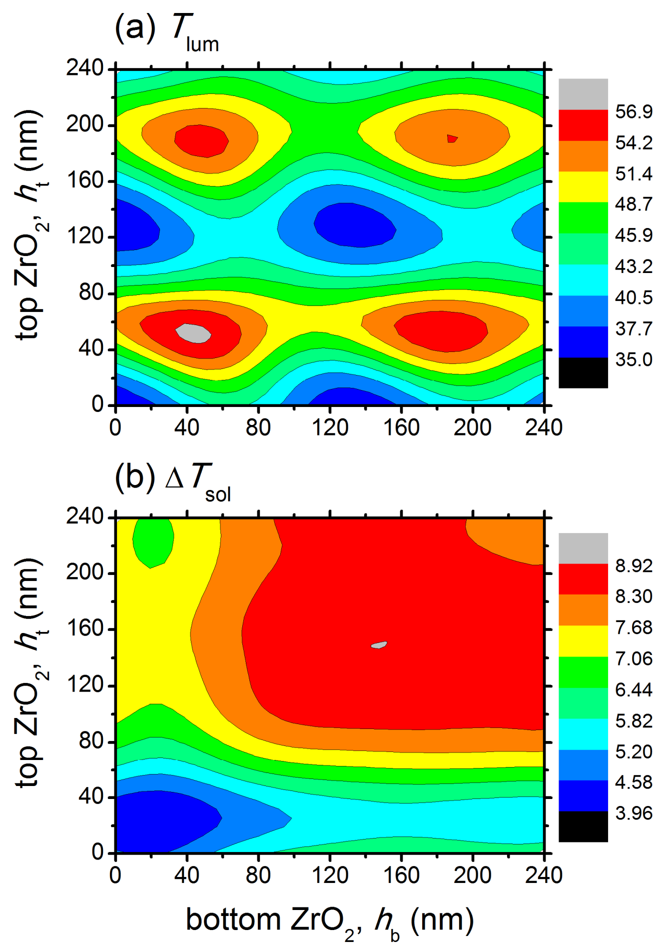
2nd order maximum of T_{lum} (ZrO_2 thickness of ≈180 nm) corresponds to **high ΔT_{sol}**

Recommendation almost independent of the beam angle

0° beam



45° beam

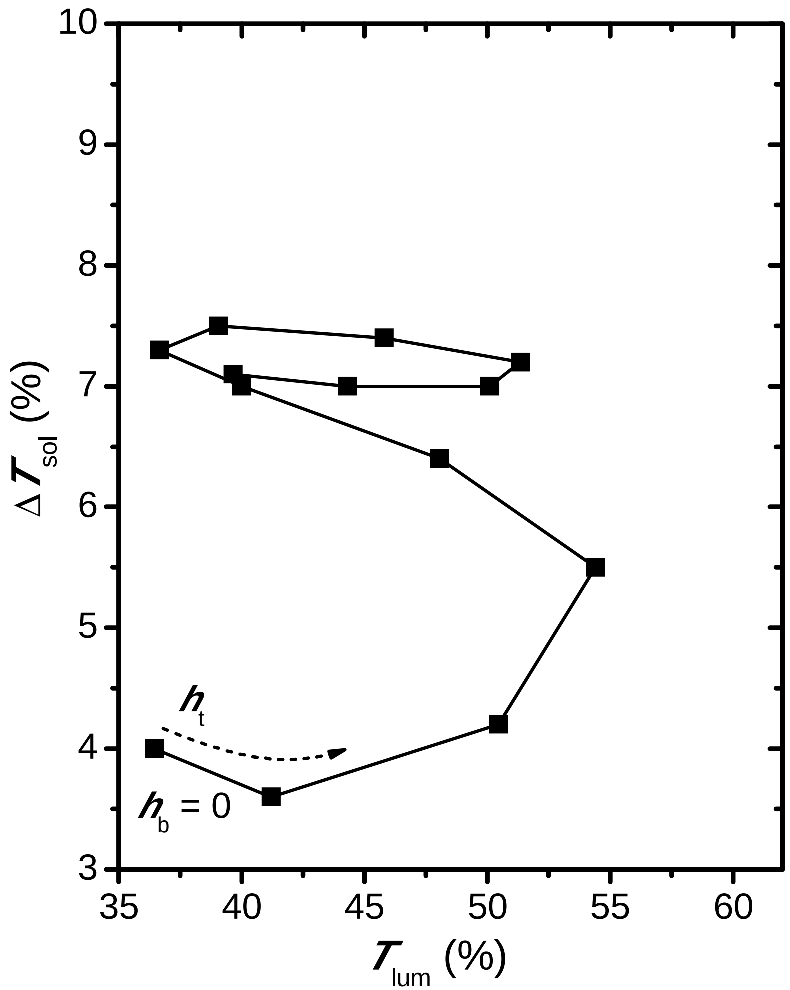


refraction towards normal: 45° in air = 19° in ZrO_2

$\cos 19° = 0.95 \Rightarrow$ 190 instead of 180 nm

How to maximize T_{lum} and ΔT_{sol} (at h_{therm} = 50 nm)

2nd order antireflection layers ⇒ improves both T_{lum} and ΔT_{sol}

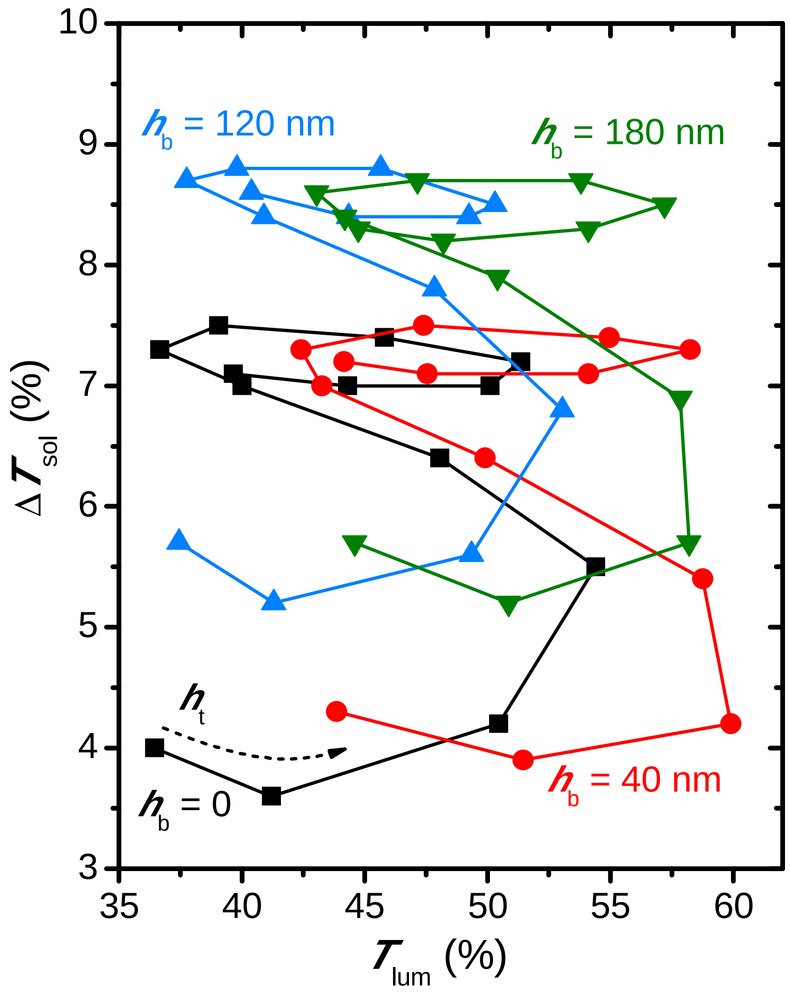


1st order maximum of T_{lum} (ZrO_2 thickness of ≈40 nm) corresponds to **low ΔT_{sol}** (handle of lasso)

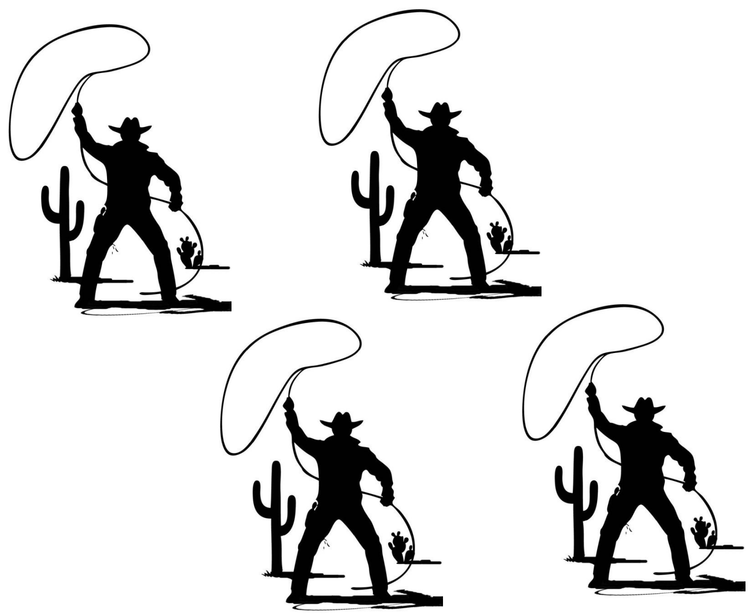
2nd order maximum of T_{lum} (ZrO_2 thickness of ≈180 nm) corresponds to **high ΔT_{sol}** (loop of lasso)

How to maximize T_{lum} and ΔT_{sol} (at h_{therm} = 50 nm)

2nd order antireflection layers ⇒ improves both T_{lum} and ΔT_{sol}



recommendation (lasso-like dependence) valid for any thickness of the other AR layer ⇒ both AR layers should be second order



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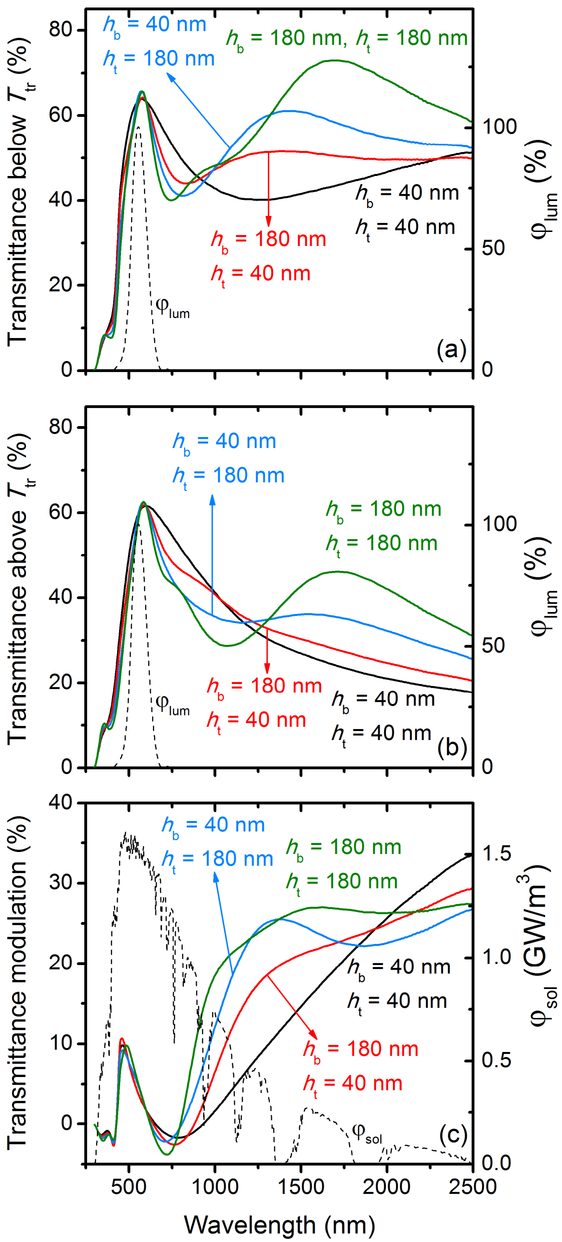
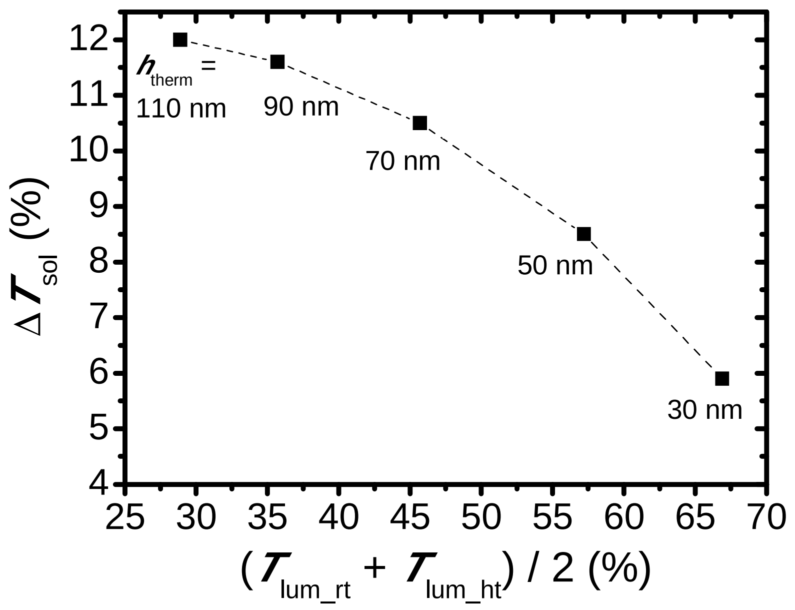


$h_b = h_t$ = 40 nm (1. order max.): high transmittance modulation only at high λ (>> 2000 nm), i.e. multiplied by low solar intensity

$h_b = h_t$ = 180 nm (2. order max.): high transmittance modulation at medium λ (wide range 800-2000 nm), i.e. multiplied by high solar intensity

in other words: optimum antireflection layers actually harm ΔT_{2500}, but improve the integral quantity ΔT_{sol}

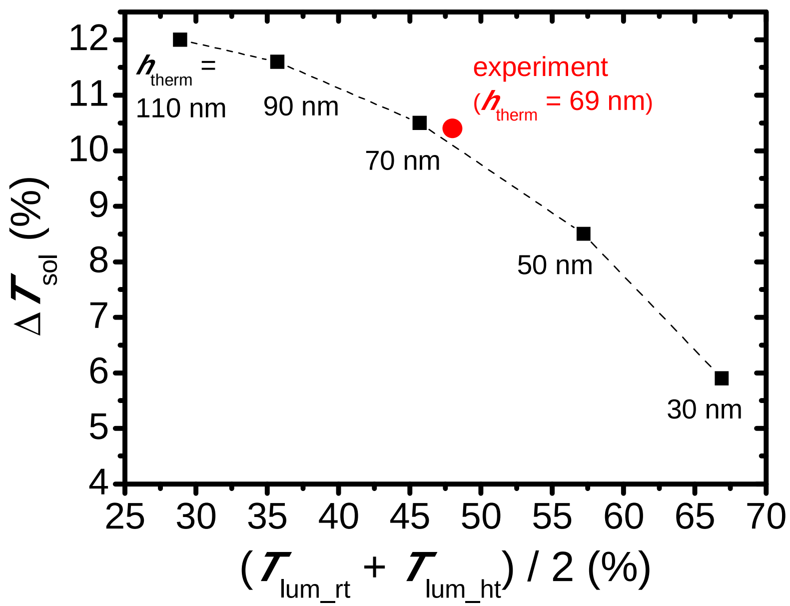
Maximize T_{lum} and ΔT_{sol} - experimental verification



Tradeoff between T_{lum} and ΔT_{sol} (depending on VO_2 thickness)

figure for optimum thickness of AR ZrO_2:
$h_b = h_t = 180$ nm

Maximize T_{lum} and ΔT_{sol} - experimental verification



Tradeoff between T_{lum} and ΔT_{sol} (depending on VO_2 thickness)

VO_2 (actually $V_{0.982}W_{0.018}O_2$) thickness h_{therm} = 69 nm: agreement with prediction

figure for optimum thickness of AR ZrO_2: $h_b = h_t$ = 180 nm

Experimental values
T_{lum} = 48%
ΔT_{sol} = 10.4%
transition at 20°C due to $W_{0.018}$

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W doping

Thermochromic transition temperature T_{tr}
(maximum derivative of T_{2500},
average over heating and cooling)

Literature:
doping by W decreases T_{tr} at the cost of T_{lum} and/or ΔT_{sol}

Presented deposition technique:
doping by W decreases T_{tr} at preserved (high) T_{lum} and ΔT_{sol}

bulk VO_2 (lit.) T_{tr} = 68°C
film VO_2 T_{tr} = 57°C
$V_{0.988}W_{0.012}O_2$ T_{tr} = 39°C *J. Houska et al., Sol. Energy Mater. Sol. Cells 191, 365-371 (2019)*
$V_{0.982}W_{0.018}O_2$ T_{tr} = 20°C *J. Vlcek et al., Sci. Rep., submitted (2019)*

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$V_{0.988}W_{0.012}O_2$	T_{tr} = 39°C
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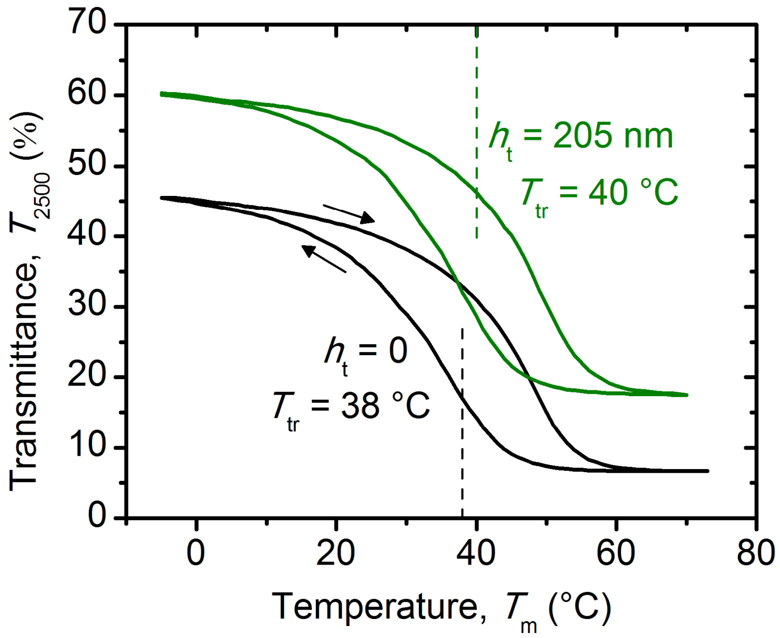
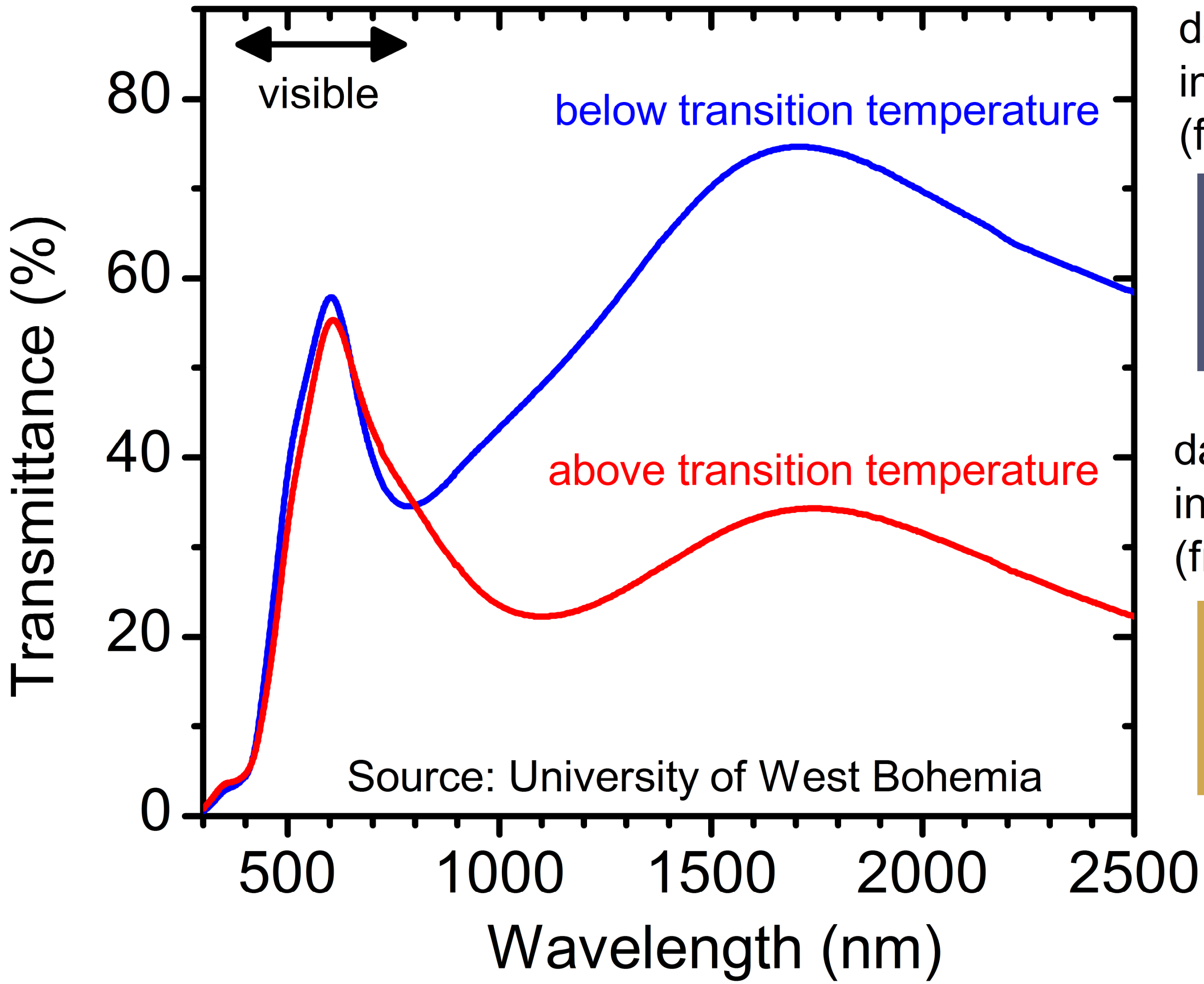
AR layer also does not harm properties (e.g. T_{tr} = 39±1 °C for $V_{0.988}W_{0.012}O_2$)



Colors

$ZrO_2/V_{0.982}W_{0.018}O_2/ZrO_2$ with h_{therm} = 69 nm and T_{tr} = 20°C



daylight color in reflection (from street)

daylight color in transmission (from inside)

Conclusions

Thermochromic VO_2 prepared under highly industry-friendly conditions (on amorphous glass, no bias, low temperature)

Optimum coating design
1^{st} order antireflection layers $\Rightarrow$ tradeoff between T_{lum} and ΔT_{sol}
2^{nd} order antireflection layers $\Rightarrow$ improves both T_{lum} and ΔT_{sol}

Optimum way of doping by W
decreases T_{tr} towards room temp. at preserved T_{lum} and ΔT_{sol}