

Design of high-performance VO₂-based thermochromic coatings, and pathway for their low-*T* preparation

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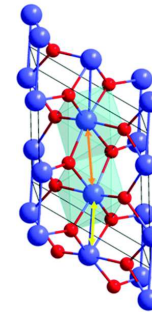
Acknowledgment

Grant Agency of the Czech Republic through Project No. 17-08944S

Thermochromic VO₂

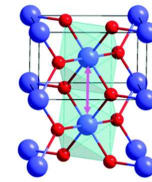
Low temperature (monoclinic):

- semiconductor (band gap)
- transparent
- low electrical and thermal conductivity



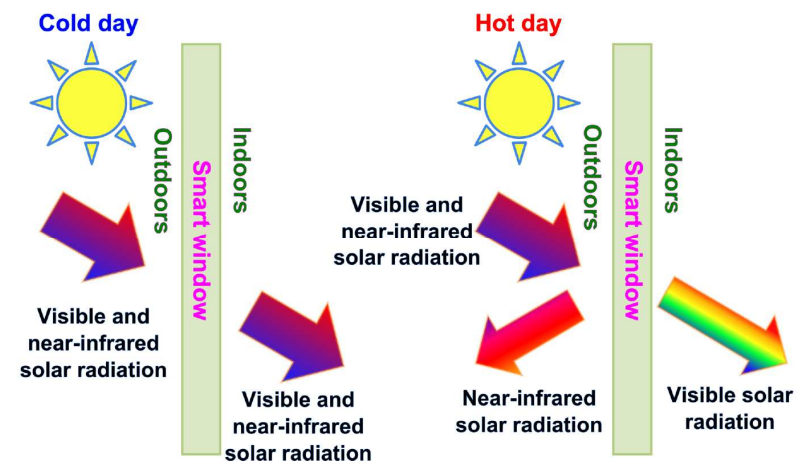
High temperature (tetragonal rutile):

- 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, ...



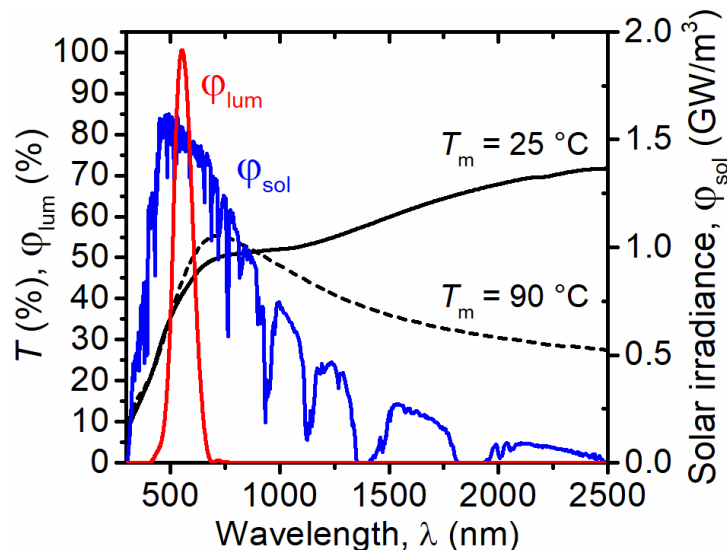
Challenges

Prepare VO₂ films by industry-friendly technique

- low temperature ($\leq 300^\circ\text{C}$ 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}



$$T_{\text{lum}} = \frac{\int_{380}^{780} \phi_{\text{lum}}(\lambda) \phi_{\text{sol}}(\lambda) T(\lambda, T_m) d\lambda}{\int_{380}^{780} \phi_{\text{lum}}(\lambda) \phi_{\text{sol}}(\lambda) d\lambda}$$

$$T_{\text{sol}} = \frac{\int_{300}^{2500} \phi_{\text{sol}}(\lambda) T(\lambda, T_m) d\lambda}{\int_{300}^{2500} \phi_{\text{sol}}(\lambda) d\lambda}$$

Outline

How to prepare VO₂ on amorphous unbiased glass at 300°C

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

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

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What is the optimum design of VO₂-based multilayers (parallel optimization of T_{lum} and ΔT_{sol})

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Control of transition temperature by W doping (without concession in terms of T_{lum} and ΔT_{sol})

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Deposition technique

High power impulse magnetron sputtering
of V in Ar+O₂ 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)

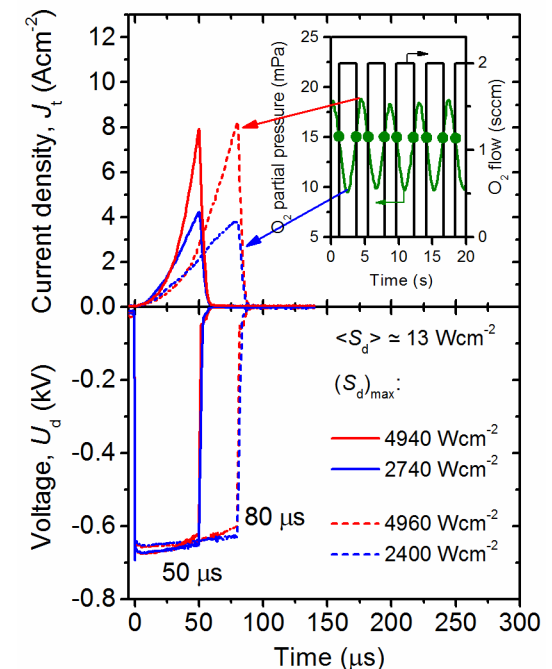
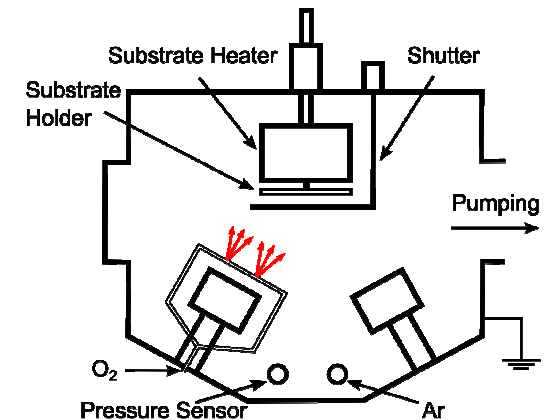
Pulsed reactive gas flow control
(European patent 2015)



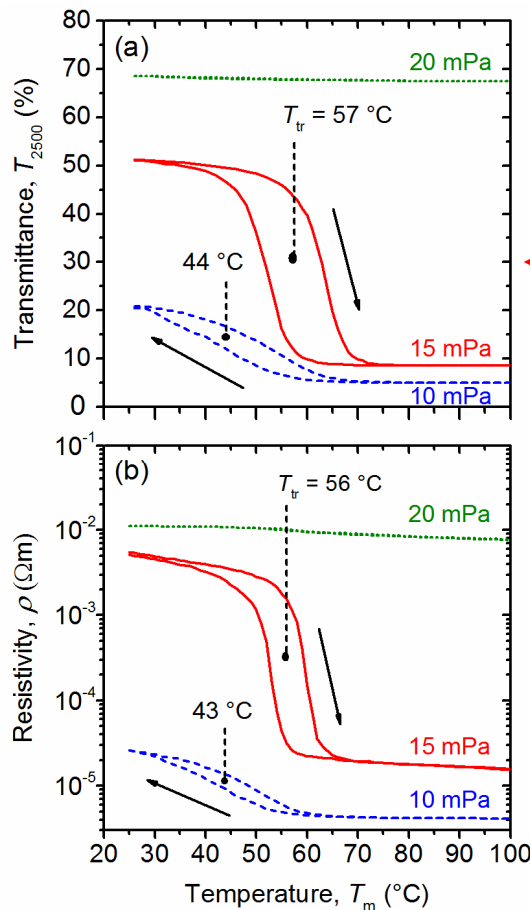
exactly as much oxygen as we need



VO₂ film stoichiometry ($\times V_2O_5$, $\times V_2O_3$)



Narrow windows for critical process parameters

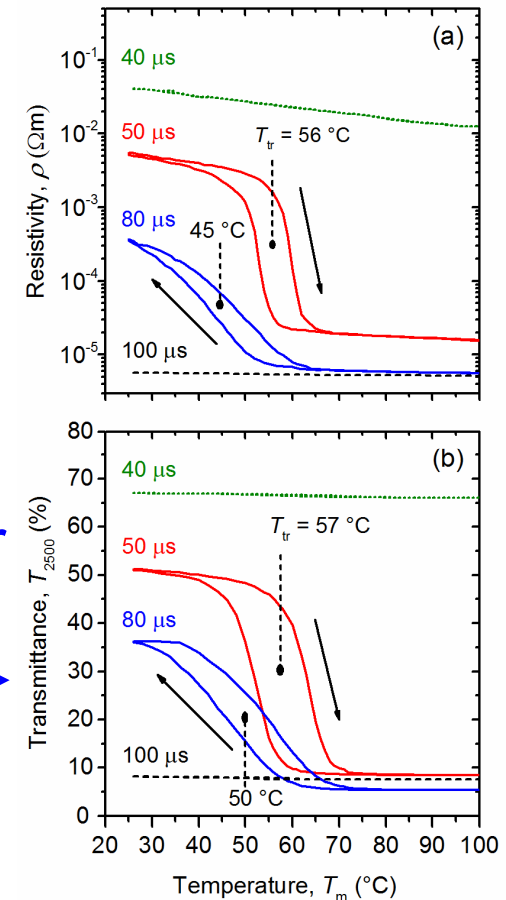


Narrow window ($\pm 10\%$) of critical O_2 pressures leading to crystalline thermochromic VO_2 ($\times V_2O_5$, V_2O_3 , etc.)

Cross-check by XRD and Raman (not shown)

O_2 window closes from $\pm 10\%$ to zero at improper voltage pulse duration

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



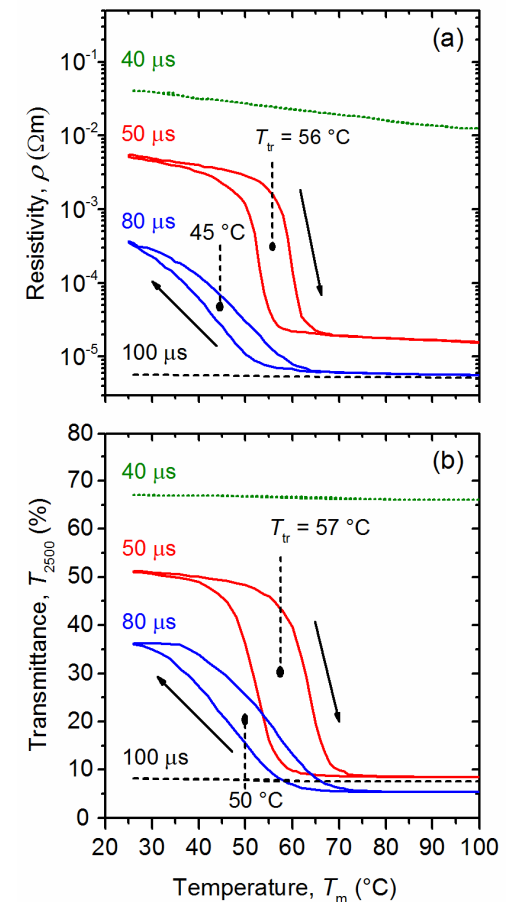
Narrow windows for critical process parameters

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

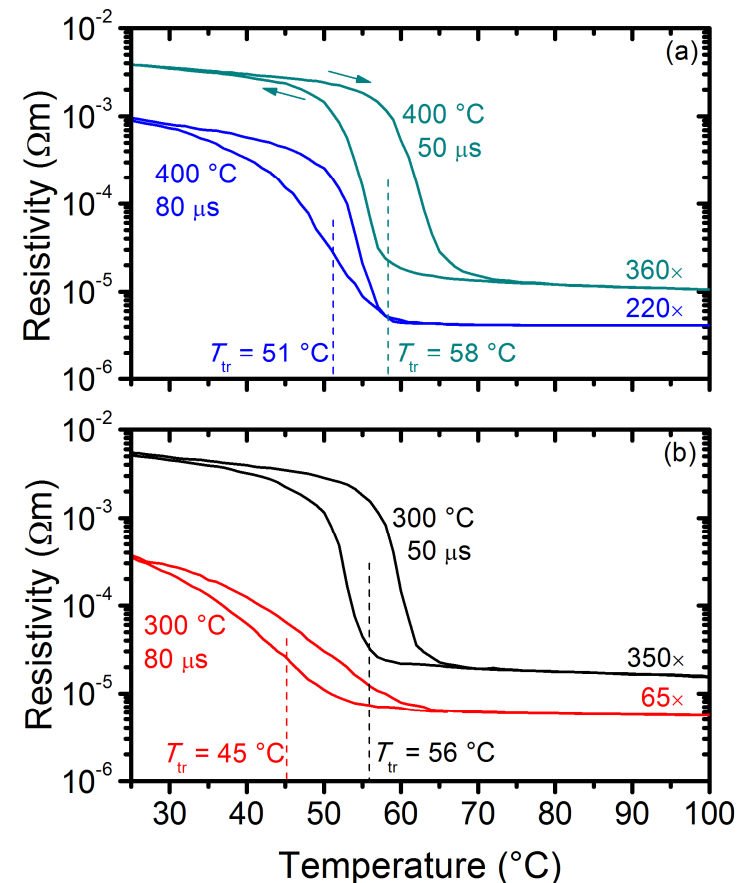
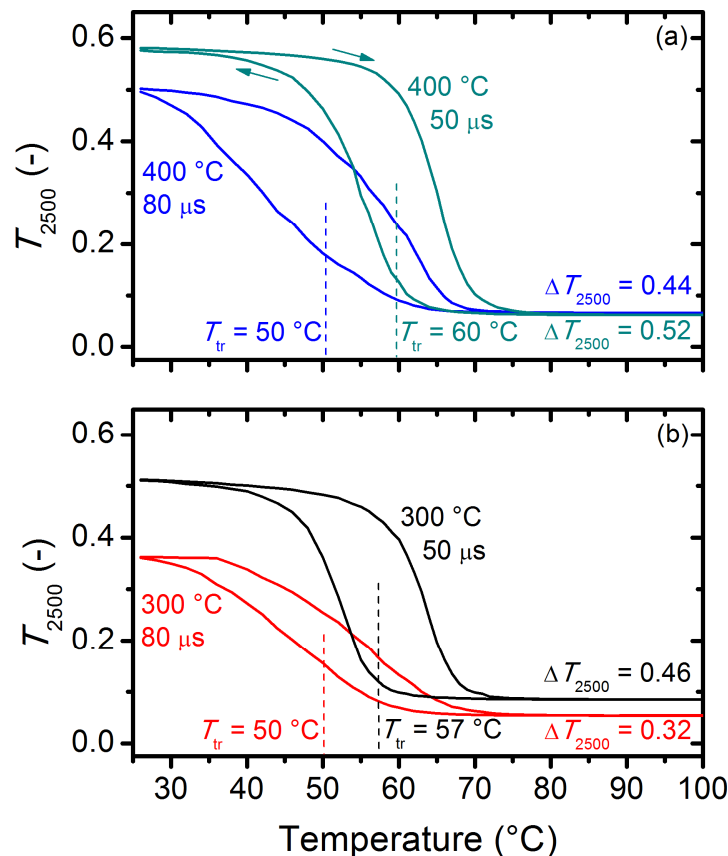
Amorphous substrate: must use sufficiently
short pulse length leading to crystallinity
(regardless slightly suboptimum composition)



Properties of VO₂ prepared at 300°C on unbiased glass

Sufficiently short (50 μ s) pulses \Rightarrow crystallinity due to ion bomb.
 \Rightarrow lowering T from 400 to 300°C does not harm the properties

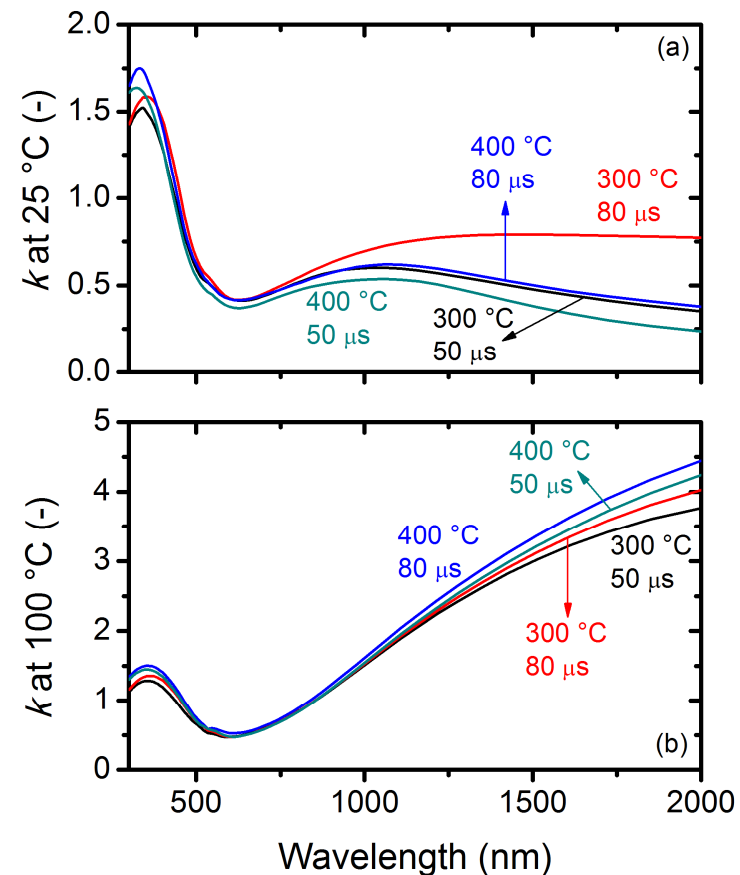
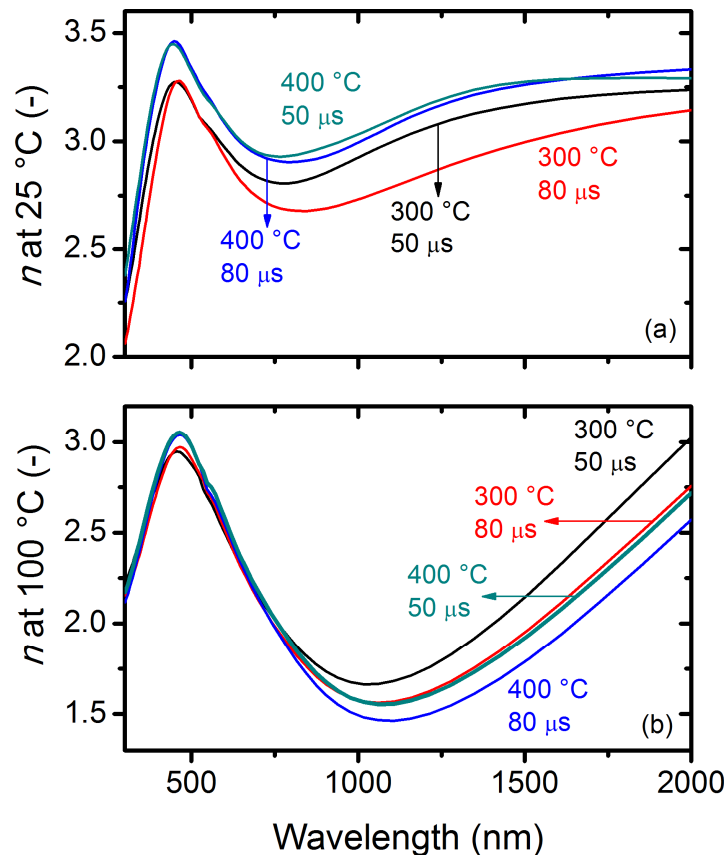
Longer (80 μ s) pulses \Rightarrow composition even closer to VO₂,
but worse crystallinity especially at 300 °C



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How to maximize T_{lum} and ΔT_{sol}

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

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

Varying VO₂ thickness \Rightarrow tradeoff
(thin films have high T_{lum} , thick films have high ΔT_{sol})

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(thin films have high T_{lum} , thick films have high ΔT_{sol})

1st order antireflection layers \Rightarrow tradeoff

(first-order maximum of T_{lum} overlaps with minimum of ΔT_{sol})

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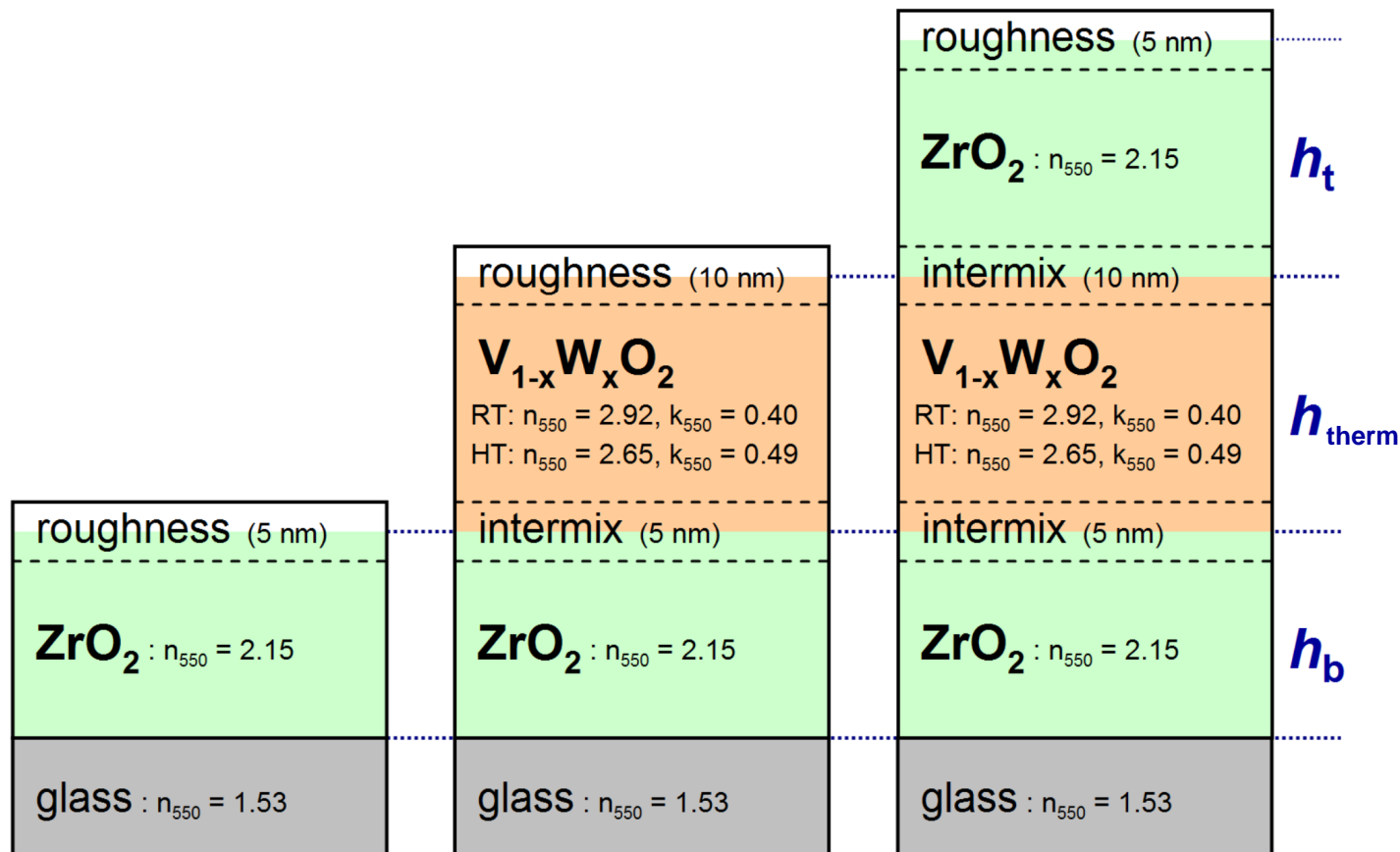
2nd order antireflection layers \Rightarrow improves both T_{lum} and ΔT_{sol}

How to maximize T_{lum} and ΔT_{sol}

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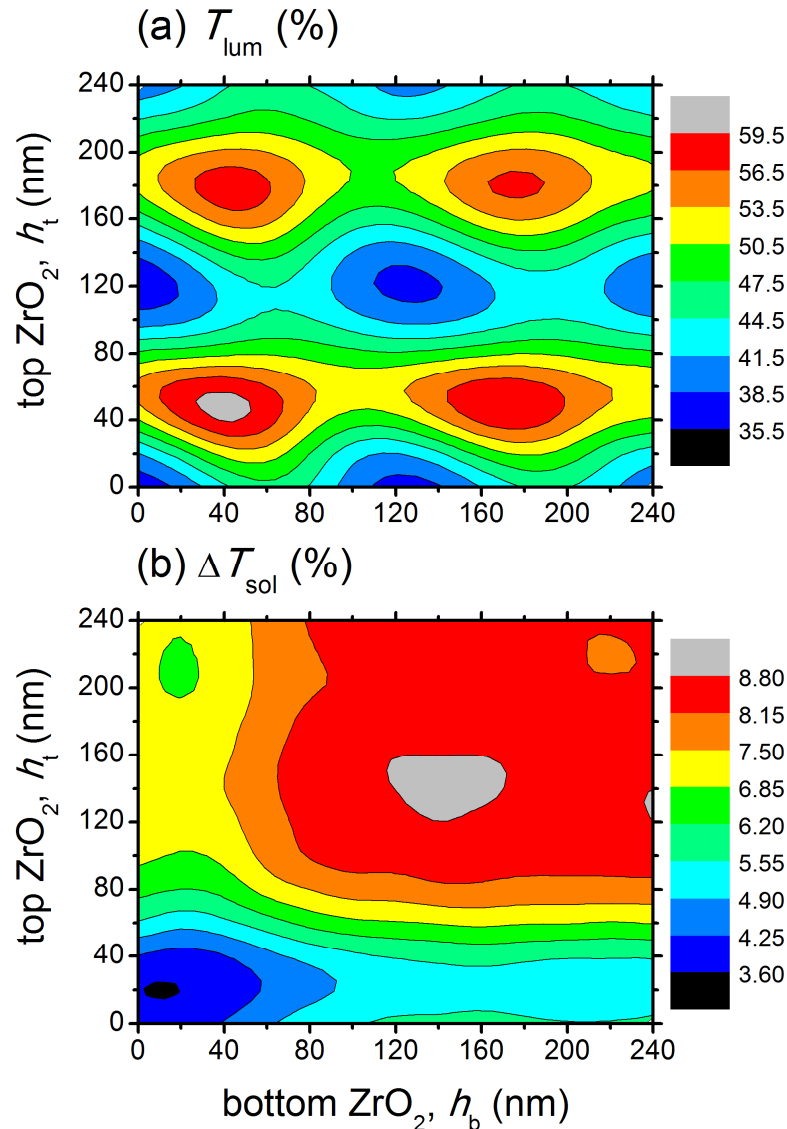
chosen material of antireflection layers: ZrO_2

chosen VO_2 or $\text{V}_{1-x}\text{W}_x\text{O}_2$ thickness in calculations below: 50 nm



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

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

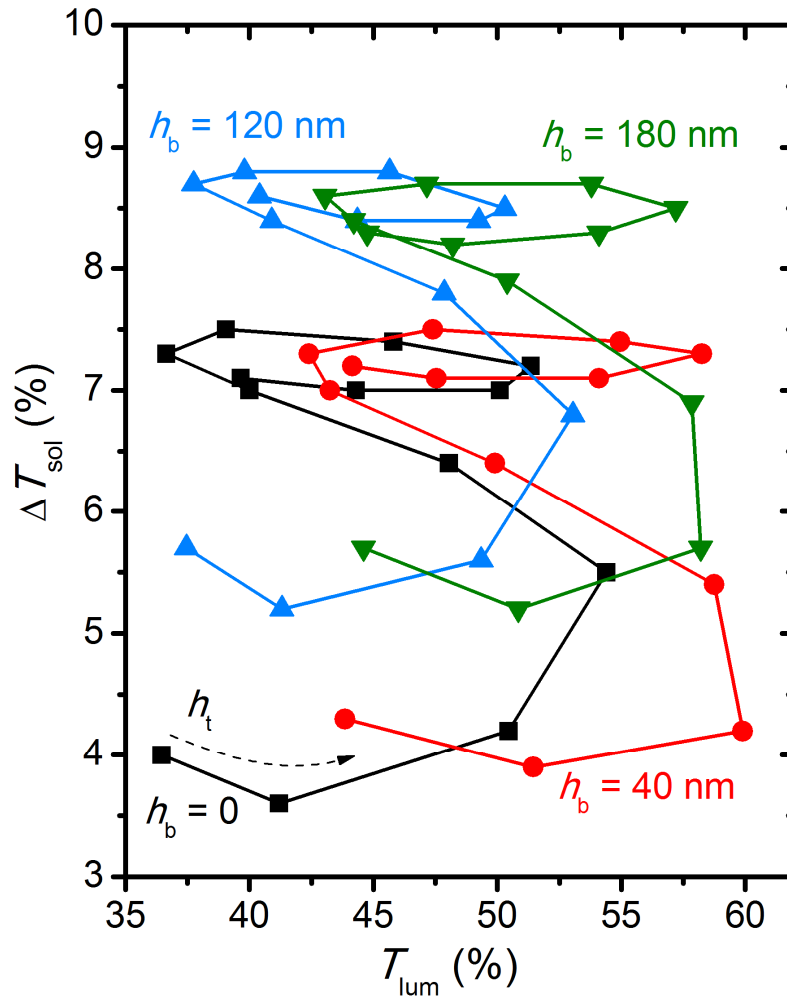


1st order maximum of T_{lum}
(ZrO_2 thickness of ≈ 40 nm)
corresponds to **low** ΔT_{sol}

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

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

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

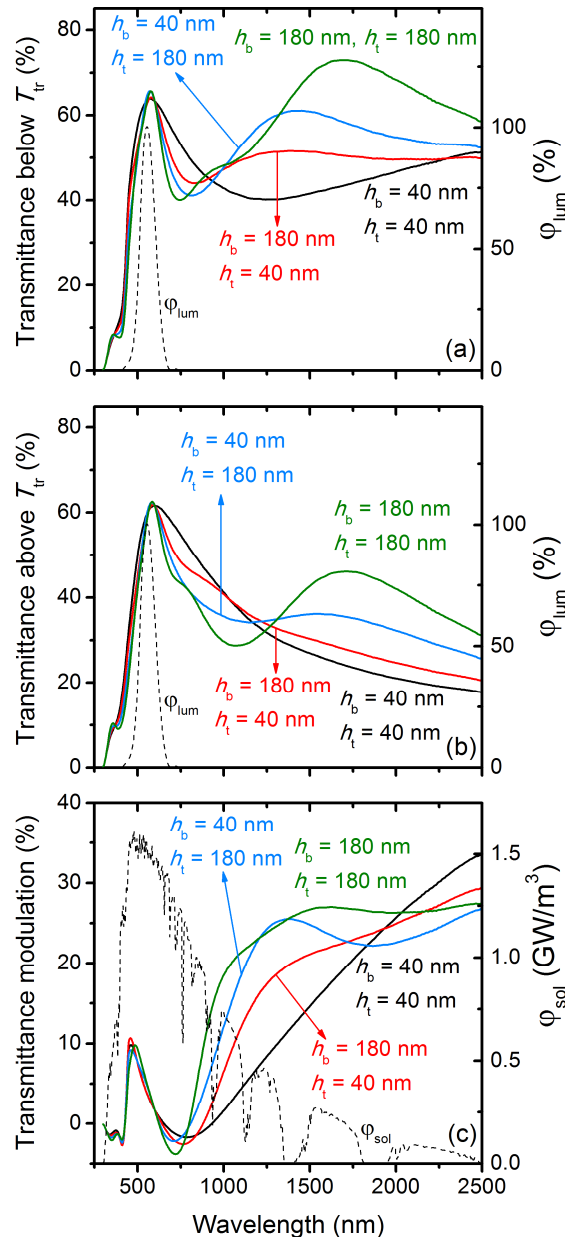


1st order maximum of T_{lum}
(ZrO₂ thickness of $\approx 40 \text{ nm}$)
corresponds to **low** ΔT_{sol}
(handle of lasso)

2nd order maximum of T_{lum}
(ZrO₂ thickness of $\approx 180 \text{ nm}$)
corresponds to **high** ΔT_{sol}
(loop of lasso)



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

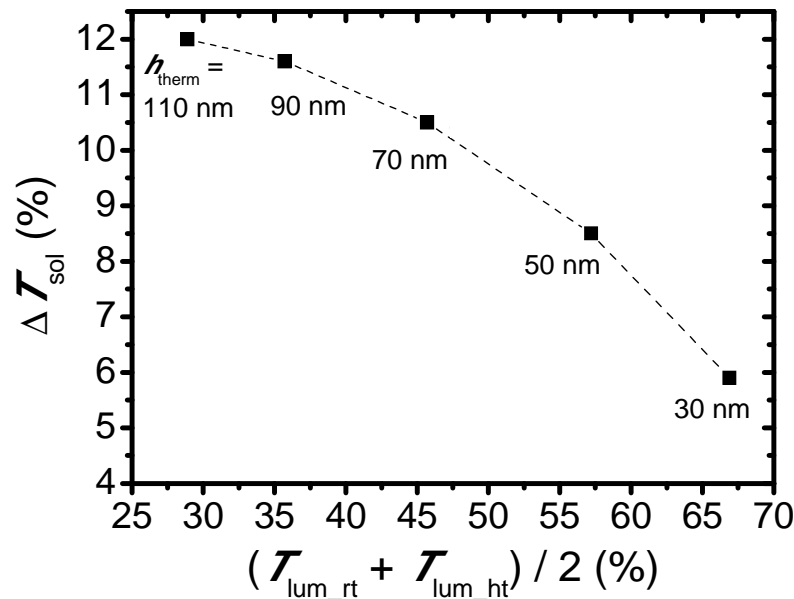


$h_b = h_t = 40$ nm (1. order max.):
high transmittance modulation
only at high λ ($>> 2000$ nm), i.e.
multiplied by low solar intensity

$h_b = h_t = 180$ 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 :
 $h_{\text{b}} = h_{\text{t}} = 180 \text{ nm}$

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

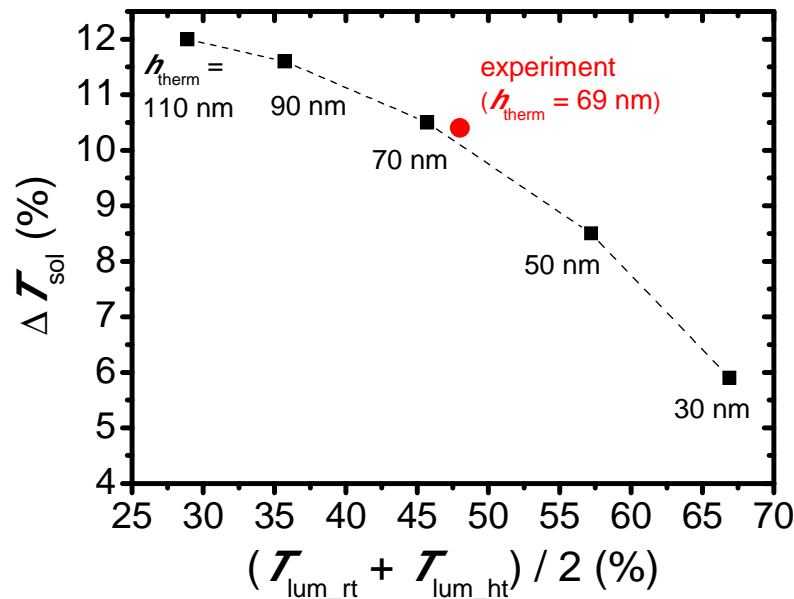


figure for optimum thickness of AR ZrO_2 :
 $h_b = h_t = 180$ nm

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

VO_2 (actually $\text{V}_{0.982}\text{W}_{0.018}\text{O}_2$)
 thickness $h_{\text{therm}} = 69$ nm:
 agreement with prediction

Experimental values

$T_{\text{lum}} = 48\%$

$\Delta T_{\text{sol}} = 10.4\%$

transition at 20°C due to $\text{W}_{0.018}$

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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.) $T_{tr} = 68^\circ\text{C}$

film VO_2 $T_{tr} = 57^\circ\text{C}$

$\text{V}_{0.988}\text{W}_{0.012}\text{O}_2$ $T_{tr} = 39^\circ\text{C}$

$\text{V}_{0.982}\text{W}_{0.018}\text{O}_2$ $T_{tr} = 20^\circ\text{C}$

W doping

Presented deposition technique:

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

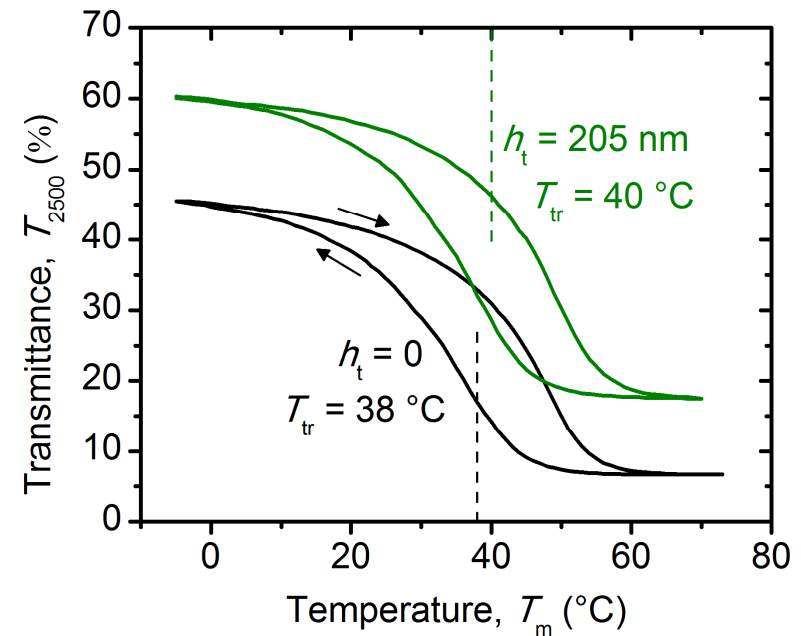
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$\text{V}_{0.988}\text{W}_{0.012}\text{O}_2$ $T_{tr} = 39^\circ\text{C}$

$\text{V}_{0.982}\text{W}_{0.018}\text{O}_2$ $T_{tr} = 20^\circ\text{C}$

AR layer also does not harm properties (e.g. $T_{tr} = 39 \pm 1^\circ\text{C}$ for $\text{V}_{0.988}\text{W}_{0.012}\text{O}_2$)



Conclusions

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

Optimum coating design

1st order antireflection layers \Rightarrow tradeoff between T_{lum} and ΔT_{sol}

2nd 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}

