

Characterization of thermochromic VO₂ thin films in a wide temperature range by spectroscopic ellipsometry

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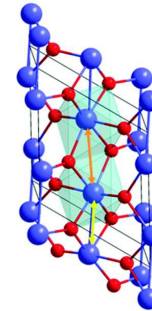
Acknowledgment

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Thermochromic VO₂

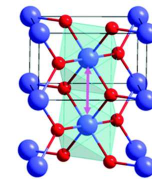
Low temperature (monoclinic):

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



High temperature (tetragonal rutile):

- metallic
- opaque
- high electrical and thermal conductivity



Smart energy-efficient window glasses,
thermal management in cars, ...



Thermochromic VO₂

Low-T semiconductor → High-T metal

Challenges

Deposition technique

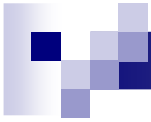
- low deposition temperature (polymers) and still crystalline
- floating substrates (no bias voltage) and still crystalline

Optimum properties

- transition temp. (literature bulk: 68 °C) close to room temp.
- high transmittance in visible
- high modulation of transmittance in NIR

Characterization

- also below room temp. (literature: only above room temp.)



Thermochromic VO₂

Low-T semiconductor → High-T metal

Challenges

Deposition technique (low T, no bias)

Optimum properties

Characterization

This work

Detailed characterization of one thin (80 nm) VO₂ film prepared under industry-friendly conditions (low T, no bias): proof that the properties are still superior

Deposition technique

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



highly ionized fluxes with many metal ions



crystallinity & densification without bias
voltage at **250 °C** (literature: ≥400 °C)

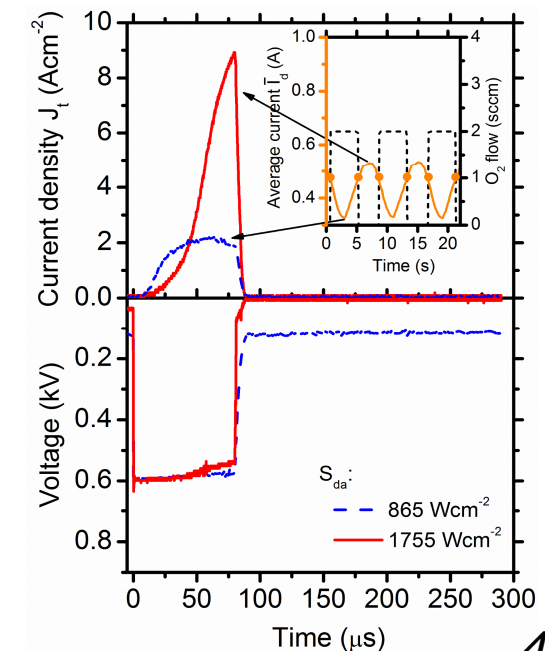
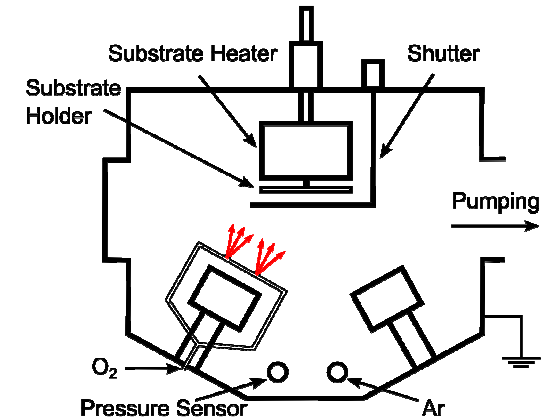
Pulsed reactive gas flow control
(European patent 2015)



exactly as much oxygen as we need



VO₂ film stoichiometry (×V₂O₅, ×V₂O₃)



Main characterization technique

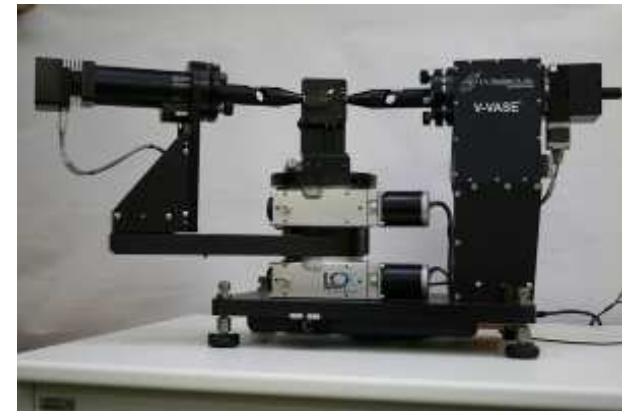
Spectroscopic ellipsometry
(J.A. Woollam VASE instrument)

Temperature-controlled stage
(ohmic heating, liquid nitrogen)

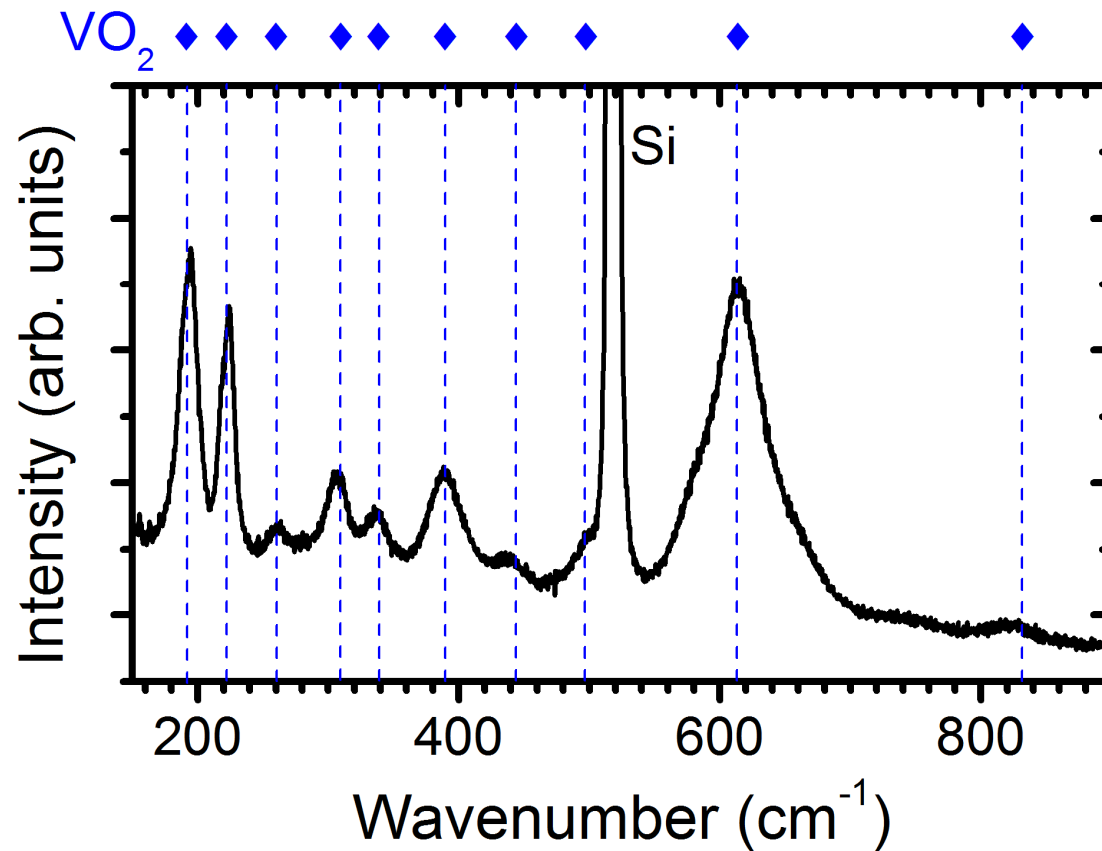
- temp. dependence at a single λ
- spectroscopic data at selected temperatures (-30 to 100 °C)

Optical model: Si substrate + VO₂ + surface roughness layer

Oscillators representing VO₂:
Cody-Lorentz + ≤ 3 Lorentz (+ Drude)

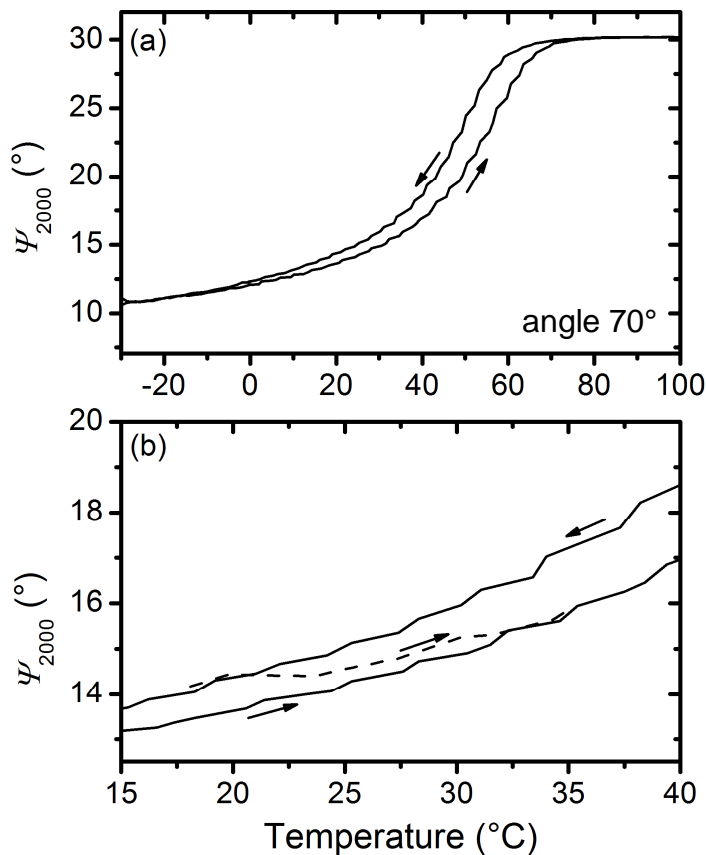


Raman spectrum of VO₂



Perfect agreement (within 3 cm⁻¹) with literature

Raw ellipsometric data - at 2000 nm



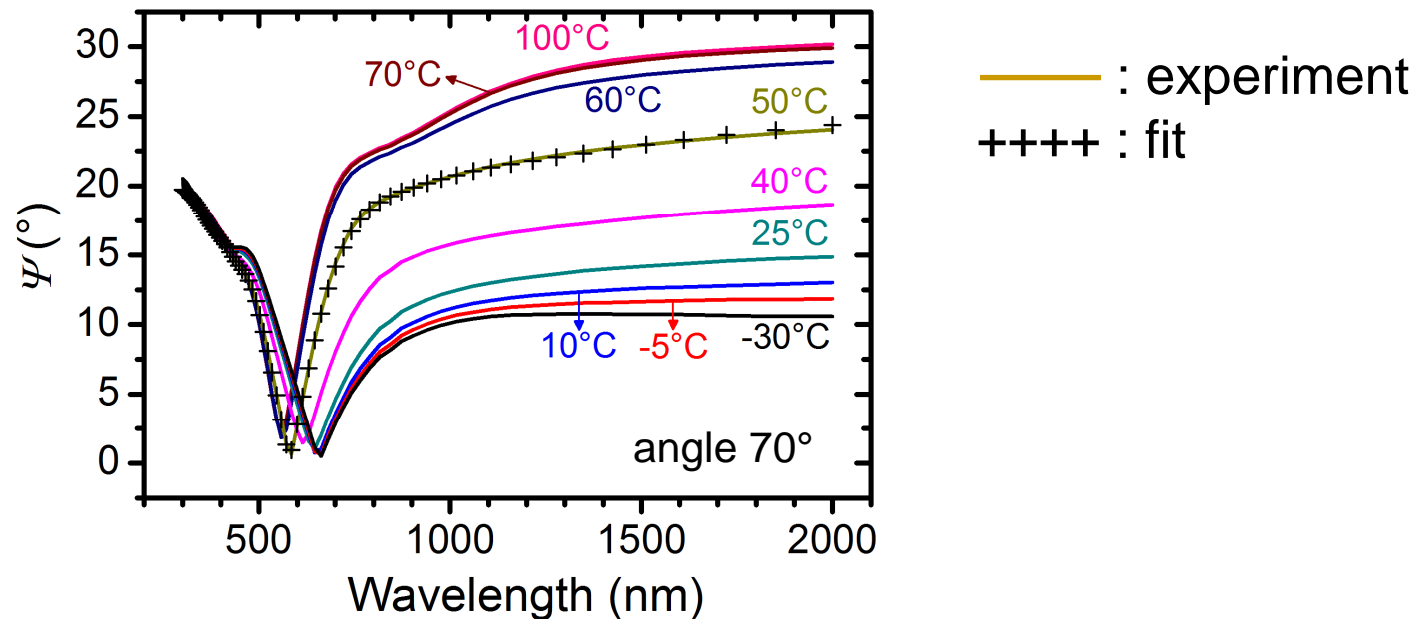
Reproducible hysteresis curve

Changes also well below the transition temperature: fixed atomic structure, but varied concentration of free charge carriers in narrow band gap (0.7 eV) semiconductor

Half of total change: 45°C
(41°C cooling, 49 °C heating)

Maximum temp. derivative: 53°C
(50°C cooling, 56°C heating)

Raw ellipsometric data - spectroscopic

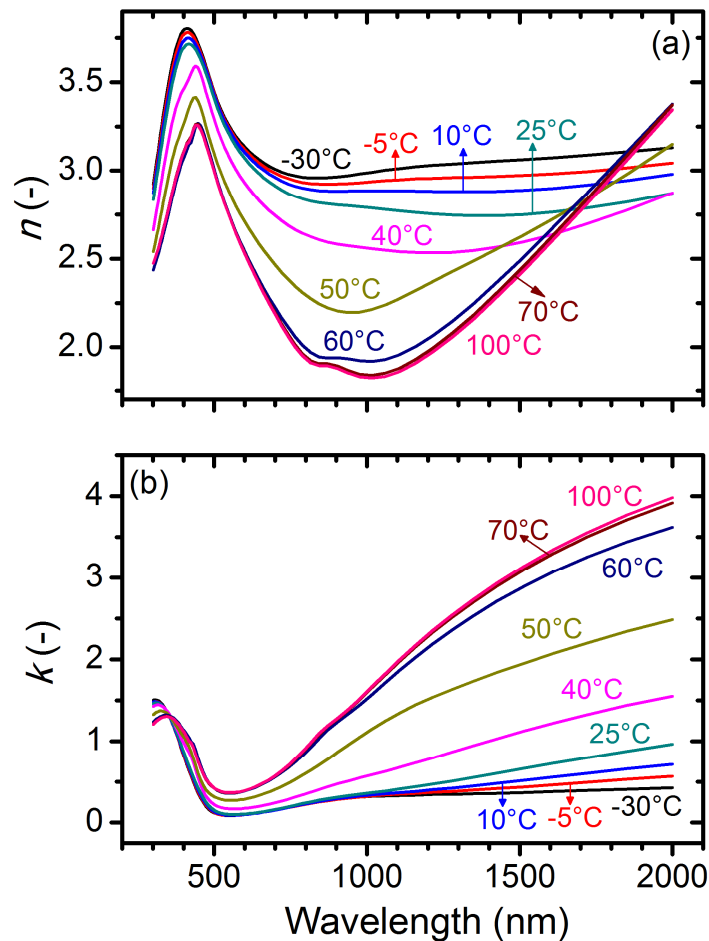


Again, fast changes around 50°C

Nice fit (Cody-Lorentz + ≤ 3 Lorentz) shown for 50°C
(HIPIMS \Rightarrow densification \Rightarrow no vertical gradient)

Basis of n , k and transmittance shown below

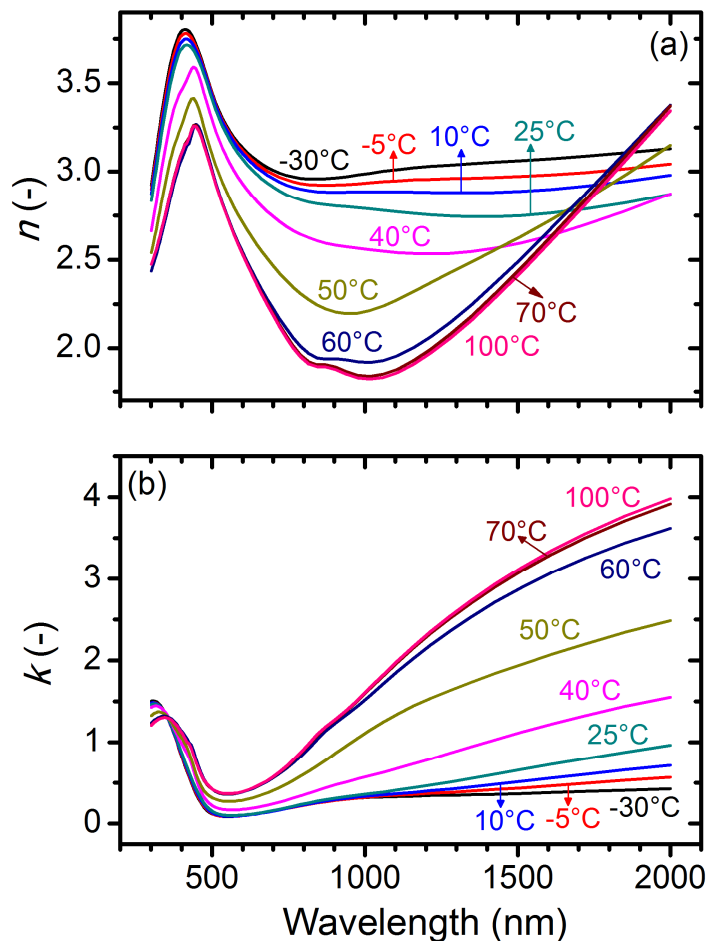
Optical constants (cooling part of hysteresis curve)



Again, fast changes around 50°C

$$\begin{aligned}
 n_{550} &= 3.24 \text{ (-30°C)} \\
 &3.20 \text{ (25 °C)} \\
 &2.73 \text{ (100 °C)} \\
 n_{2000} &= 3.13 \text{ (-30 °C)} \\
 &2.87 \text{ (25 °C) (non-monotonous)} \\
 &3.35 \text{ (100 °C)} \\
 k_{550} &= 0.085 \text{ (-30 °C)} \\
 &0.10 \text{ (25 °C)} \\
 &0.37 \text{ (100 °C)} \\
 k_{2000} &= 0.43 \text{ (-30 °C)} \\
 &0.96 \text{ (25 °C)} \\
 &3.98 \text{ (100 °C)}
 \end{aligned}$$

Optical constants (cooling part of hysteresis curve)



Again, fast changes around 50°C

$$n_{550} = \begin{matrix} 3.24 (-30^{\circ}\text{C}) \\ 3.20 (25^{\circ}\text{C}) \\ 2.73 (100^{\circ}\text{C}) \end{matrix}$$

$$n_{2000} = \begin{matrix} 3.13 (-30^{\circ}\text{C}) \\ 2.87 (25^{\circ}\text{C}) \text{ (non-monotonous)} \\ 3.35 (100^{\circ}\text{C}) \end{matrix}$$

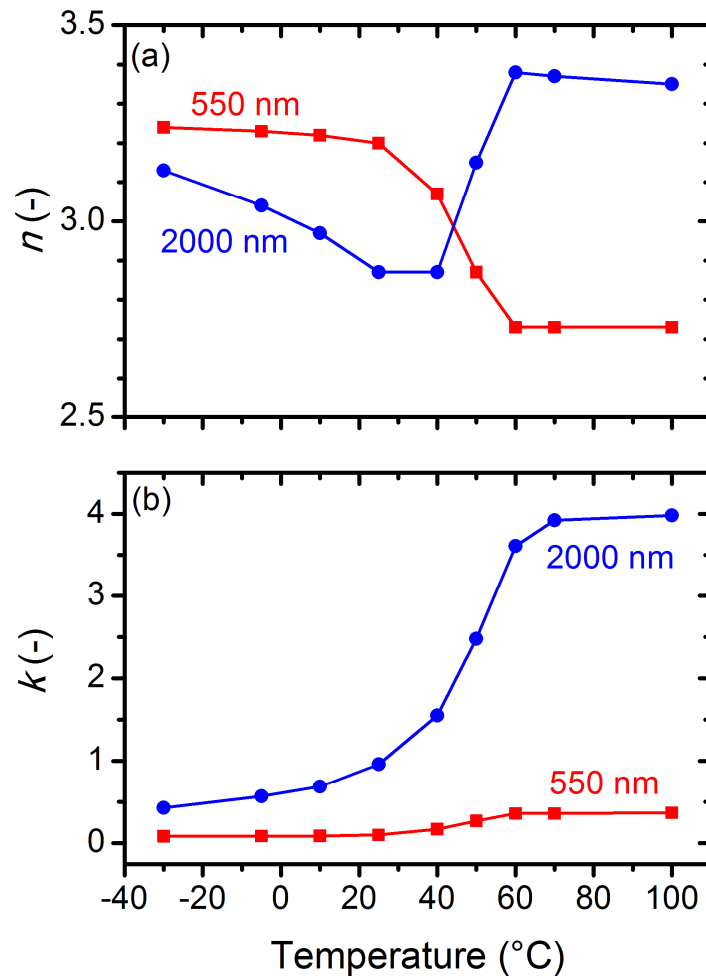
$$k_{550} = \begin{matrix} 0.085 (-30^{\circ}\text{C}) \\ 0.10 (25^{\circ}\text{C}) \\ 0.37 (100^{\circ}\text{C}) \end{matrix}$$

sufficiently
high O
content

$$k_{2000} = \begin{matrix} 0.43 (-30^{\circ}\text{C}) \\ 0.96 (25^{\circ}\text{C}) \\ 3.98 (100^{\circ}\text{C}) \end{matrix}$$

sufficiently
low O
content

Optical constants (cooling part of hysteresis curve)



Again, fast changes around 50°C

$$n_{550} = 3.24 \rightarrow 2.73$$

$$n_{2000} = 3.13 \rightarrow 2.87 \rightarrow 3.35$$

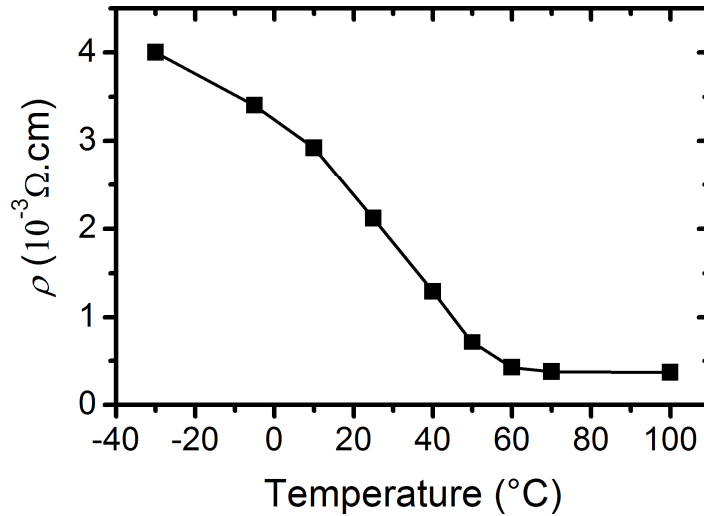
$$k_{550} = 0.085 \rightarrow 0.37$$

$$k_{2000} = 0.43 \rightarrow 3.98$$

Half of total change (k): 45°C

Max. temp. derivative (n, k): 50°C

Drude oscillator \Rightarrow (lower bound of) resistivity



Only oscillator in NIR:

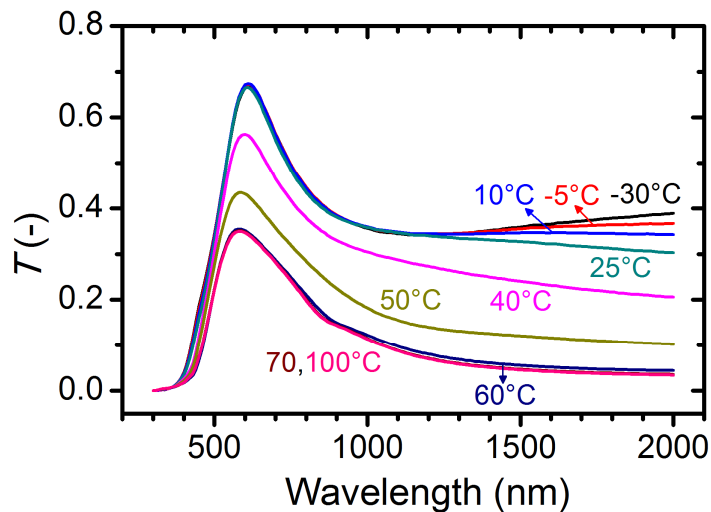
$$\epsilon_{\text{Drude}} = -1/[\rho\epsilon_0(\tau\omega^2 + i\omega)] \quad (\rho \sim 1/N\tau)$$

Oversimplification, but yields
correct trend: increasing
temperature & closing band gap



increasing N & decreasing ρ

Predicted transmittance (T) 100 nm film on 1 mm glass



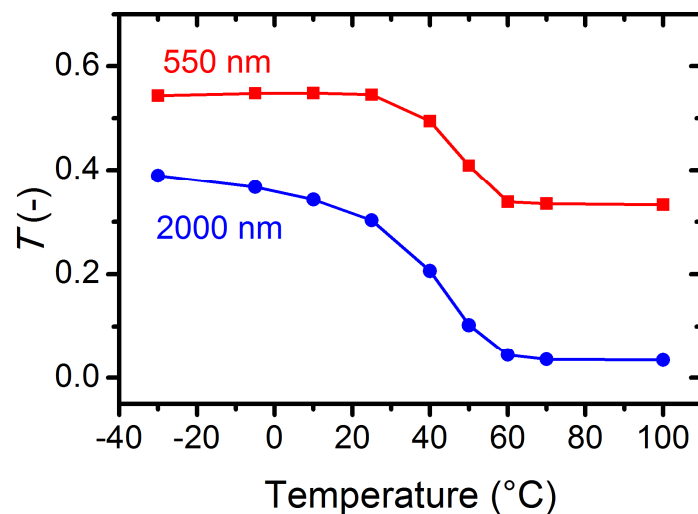
(Again: under industry-friendly
deposition conditions)

$T_{550} = 54\text{-}55\%$ (-30°C to 25°C)
 33% (100°C)

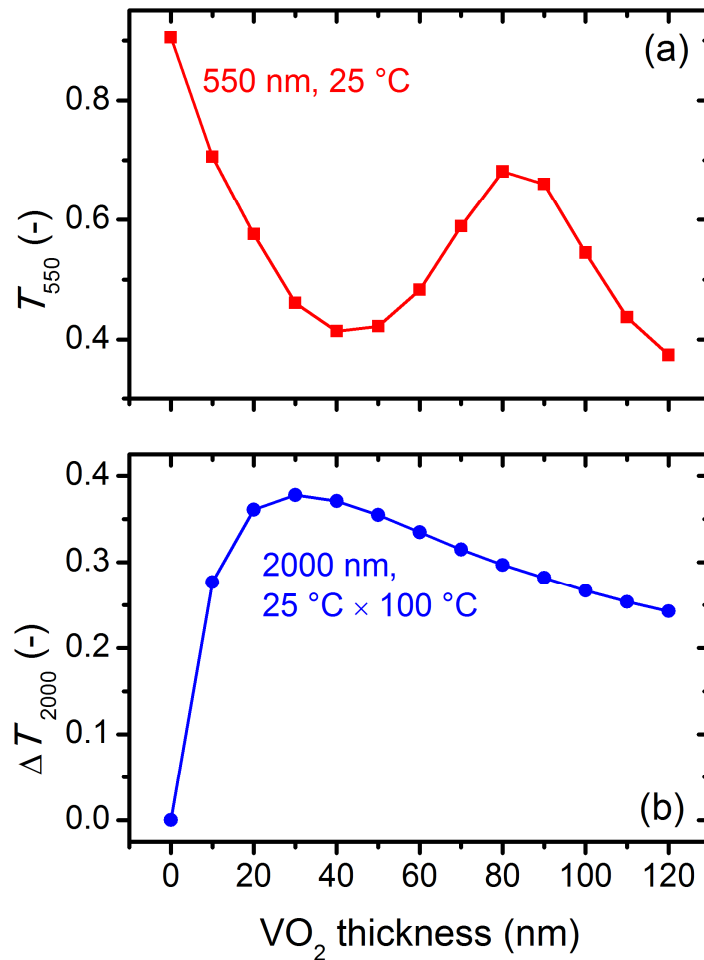
$T_{2000} = 39\%$ (-30°C)
 30% (25°C)
 3.4% (100°C)

Half of total T_{2000} change: 40°C

Max. T_{2000} temp. derivative: 45°C



Predicted transmittance (T) varied film thickness on 1 mm glass



Strong dependence of the transmittance on the constructive / destructive interference especially in the visible

Maximum NIR modulation achieved for destructive interference in the visible \Rightarrow application-dependent thickness choice

Conclusions

- Thermochromic VO₂ (high-power impulse magnetron sputtering with pulsed reactive gas flow control)
- No substrate bias, substrate temperature 250°C only
- Spectroscopic ellipsometry in a wide temperature range
temperature-dependence of $\Psi, \Delta \Rightarrow n, k \Rightarrow$ transmittance T
- Superior properties (despite the industry-friendly conditions)
 - thermochromic transition around 50°C
 - high visible T (100 nm: e.g. $T_{550} = 55\%$, $T_{600} = 67\%$)
 - high modulation of NIR T (100 nm: e.g. $T_{2000} = 39 \rightarrow 3.4\%$)

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