Unravelling the complex optical properties of heterogeneous transparent and conducting vanadates thin films grown on a 2D nanosheet layer by the means of Spectroscopic Ellipsometry

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Ref : A. Boileau *et al*, *Highly Transparent and Conductive Indium-Free Vanadates Crystallized at Reduced Temperature on Glass Using a 2D Transparent Nanosheet Seed Layer*, **Adv. Funct. Mater. 2021, 2108047**

I – Context

II – Structural properties

III – Optical properties through Effective Medium

IV – Infrared properties

IV – Conclusions

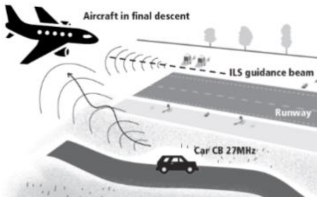
Context

Heating/defrosting elements for aircrafts

Transparent Conductive Oxides (TCOs)

Heat mirrors for functional glass

Gas sensors



Electromagnetic shielding

- Indium Tin Oxide (ITO) : best FOM and most used

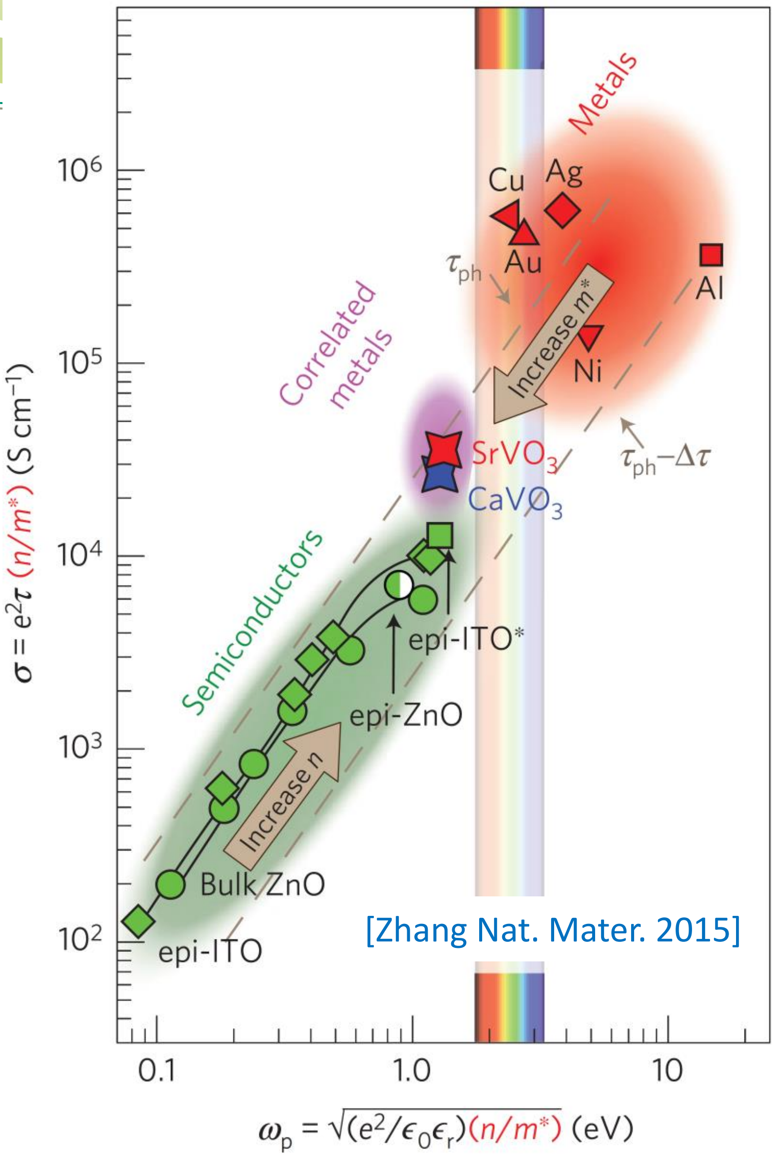
Degenerated semiconductor, $N_e \sim 10^{20}$ $e^{-}.cm^{-3}$

- Indium scarcity ➔ search for alternatives

- $CaVO_3$ and $SrVO_3$ Vanadates : as good as ITO

Metallic, $N_e \sim 10^{22}$ $e^{-}.cm^{-3}$

+ Strong correlation ➔ plasma frequency in IR range

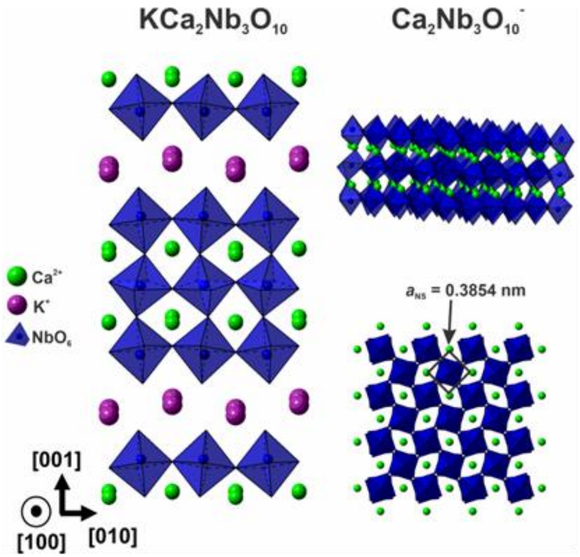


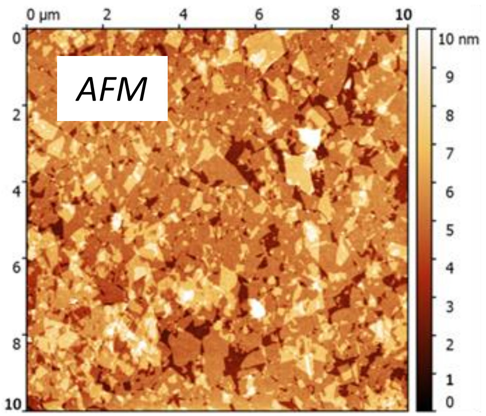
- Limitation : high-temperature epitaxial growth on specific textured substrate (STO, LSAT…)

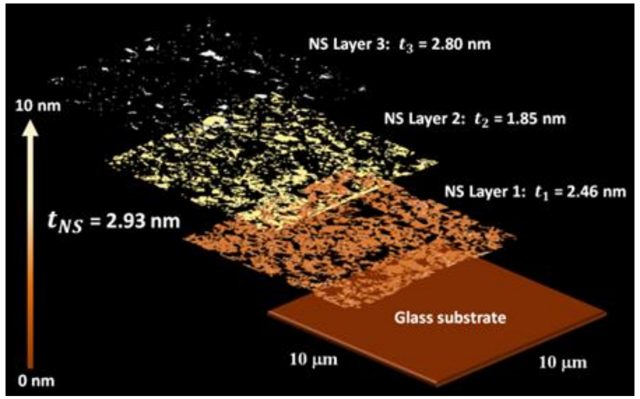
➔ How to transfer it on any substrate (e.g. glass) ??

Vanadates growth on Nanosheet template

- Nanosheet (NS) deposition by Langmuir-Blodgett :

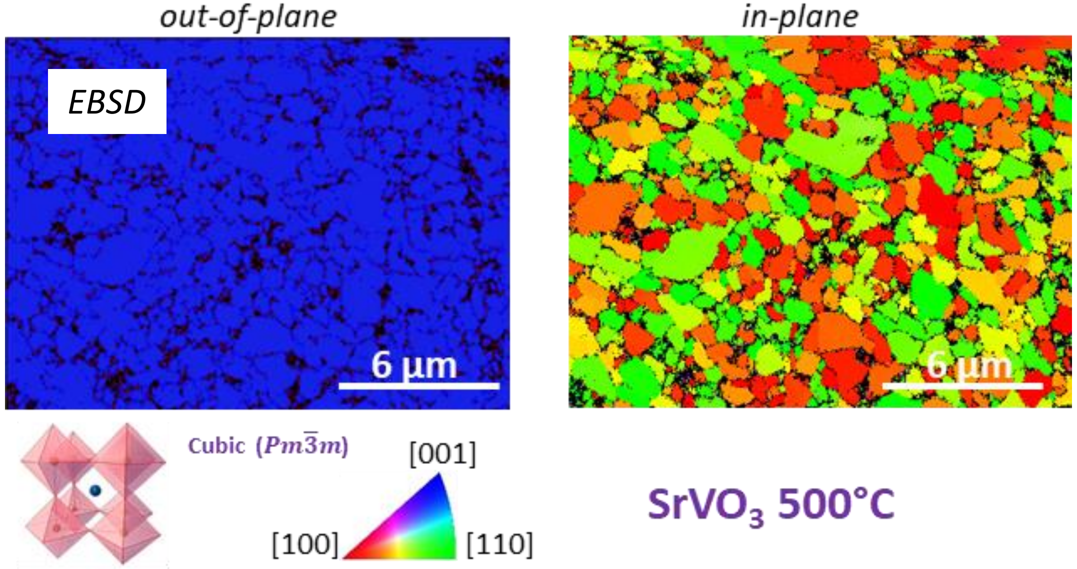


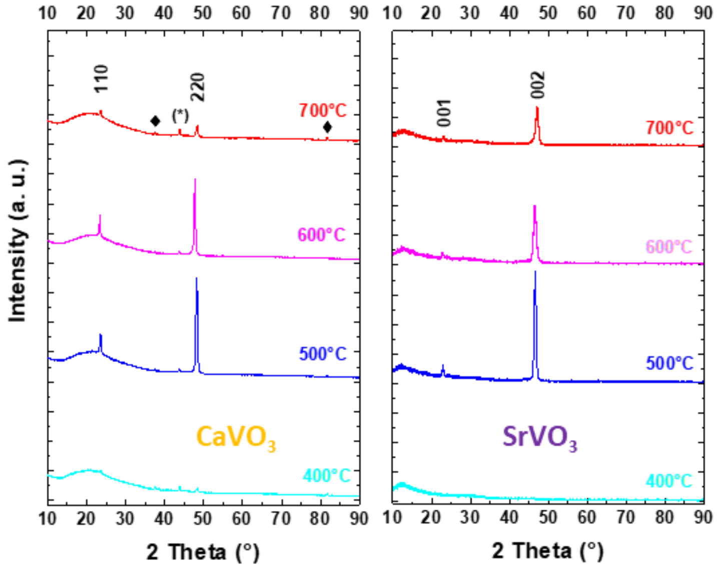




- NS coverage ~ 70 % (30 % = bare Glass substrate)
- ~ 3 NS layers

- Pulsed Laser Deposition of $CaVO_3$ / $SrVO_3$ @ 400 to 700 °C



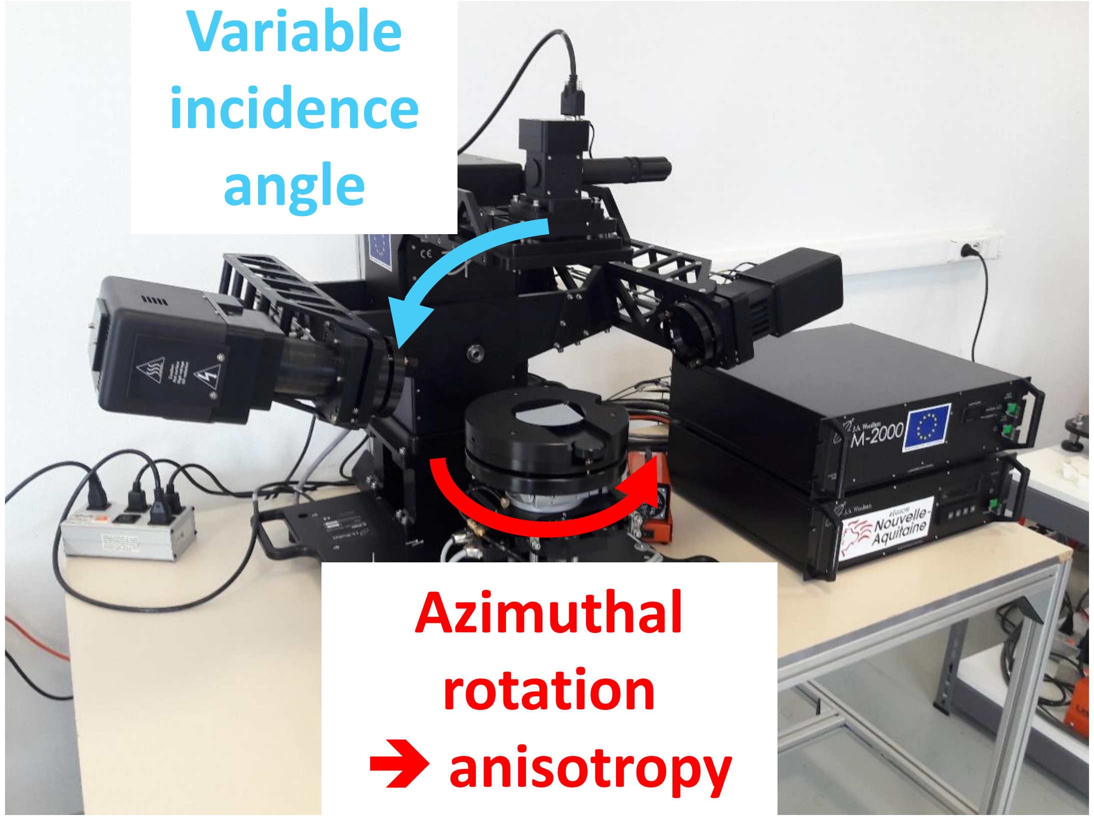


Textured epitaxial growth

Crystalline coverage ~70 %
(30 % = amorphous vanadates)

Growth temperature :
- 400 °C : amorphous
- **500-600 °C : nice cristallinity**
- 700 °C : degraded

Optical Properties : Ellipsometry @ Institut Pprime, Poitiers



Woollam M2000XI
UV-visible-NIR : 211 nm – 1700 nm

Cryostat 77 K - 500 K (vaccuum)

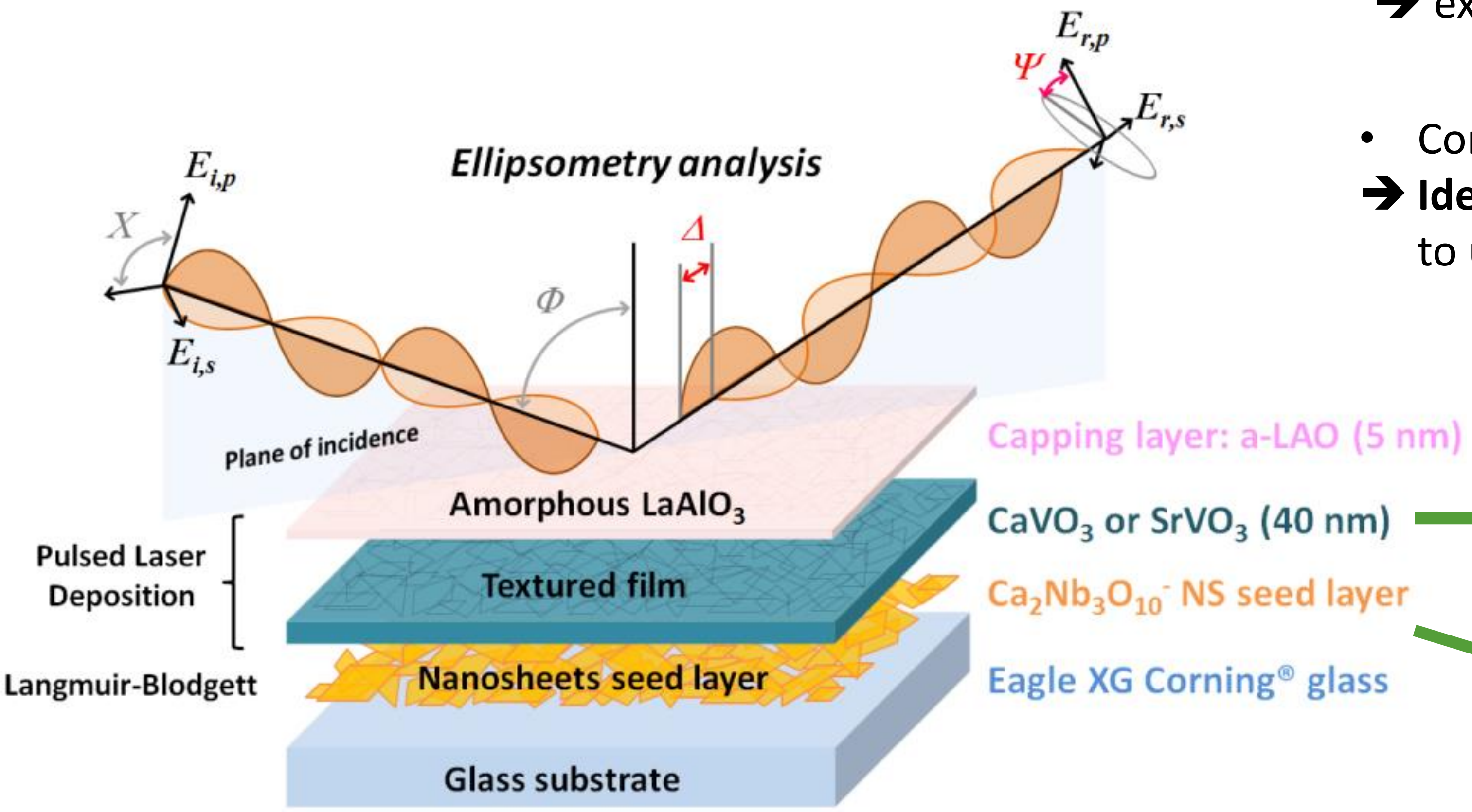
Woollam Vase-IR Mark II
IR : 1.7 µm – 40 µm

Projet
FEDER
IMATOP

Linkam Heat Cell
-70 °C to 600 °C
(UV to IR)
+ environment :
N_2, wet air, …

Optical Properties

- Sample layout :



- Spectroscopic Ellipsometry :

$$\rho = \frac{r_p}{r_s} = \tan\Psi\, e^{i\Delta}$$

➔ extract dielectric functions (DFs) $\varepsilon = \varepsilon_1 + i\varepsilon_2$

- Complex heterostructure

➔ **Identifying the optical indexes of each layer** to unravel the optical properties

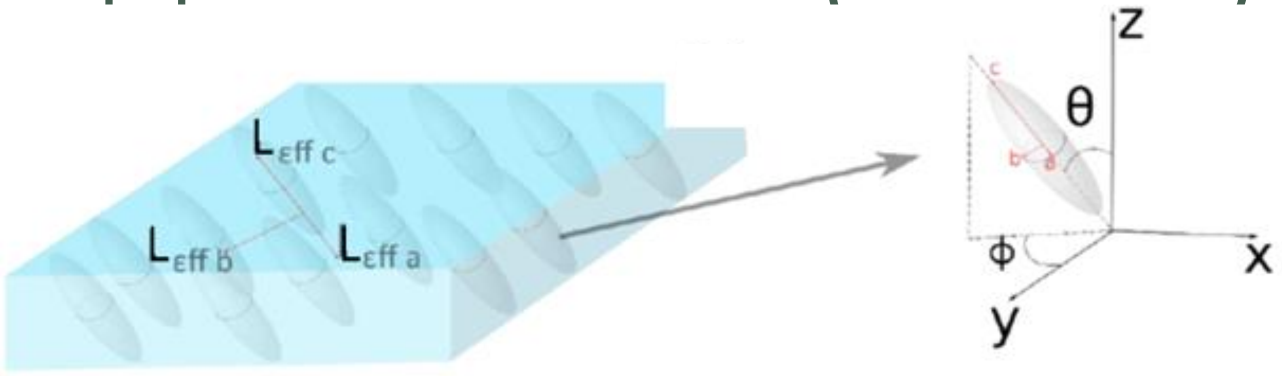
(reference sample)

- 70 % crystalline (growth on NS)
- 30 % amorphous (growth on Glass)

➔ **treat as Effective Medium**

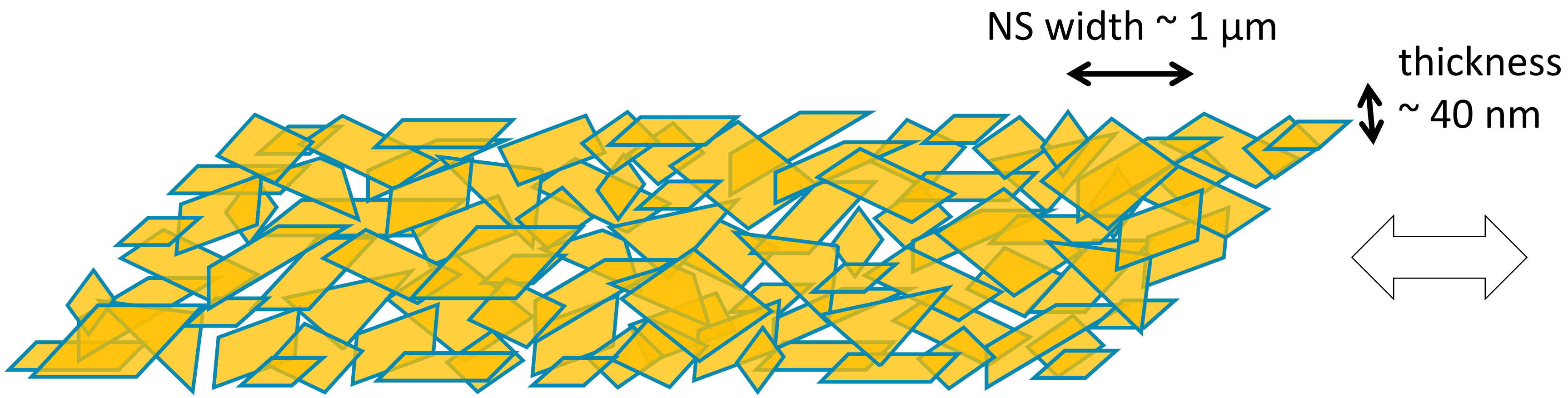
(reference sample)

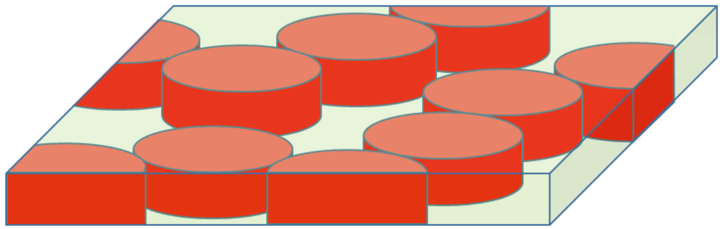
Anisotropic Bruggemann Effective Medium Approximation (ABEMA)



- Analytical model for light scattering on ellipsoidal inclusion (Depolarization factors L_x, L_y, L_z)
- Symetric : volume fraction $f = 0 - 100\ \%$

$$f\frac{1-\varepsilon_{eff,j}}{\varepsilon_{eff,j}+L_j^D(1-\varepsilon_{eff,j})} + (1-f)\frac{\varepsilon_m-\varepsilon_{eff,j}}{\varepsilon_{eff,j}+L_j^D(\varepsilon_m-\varepsilon_{eff,j})} = 0$$





$L_z = 1\,;L_x/L_y = {}^{1}/_{2}$

(Flat cylinders)

Amorphous $CaVO_3$: sample grown @ 400 °C

Layer # 3 = LAOa Cauchy Thickness # 3 = 5.40 nm

Layer # 2 = cvo 191213 400degC visir - TL GGG D Thickness # 2 = 40.20 nm

Show Dialog

- e1 Components
  - Einf = **1.238** (fit)
  - UV Pole Amp. = 0.000 UV Pole En. = 11.000
  - IR Pole Amp. = 0.000
- e2 Components
  - Oscillator Menu: **Add** **Delete** **Delete All** **Sort**
  - Fit Menu: All None Amp. Br. En.
  - 1: Type = Tauc-Lorentz Amp1 = **47.5488** (fit)
    Br1 = **1.618** (fit) Eo1 = **3.902** (fit) Eg1 = **2.773** (fit)
  - 2: Type = Drude(RT) Resistivity (Ohm·cm)2 = **0.002231** (fit) Scat. Time (fs)2 = **0.381** (fit)
  - 3: Type = Gaussian Amp3 = **4.742767** (fit) Br3 = **4.7349** (fit) En3 = 8.000
  - 4: Type = Gaussian Amp4 = **0.644681** (fit) Br4 = **8.5239** (fit) En4 = **2.173** (fit)

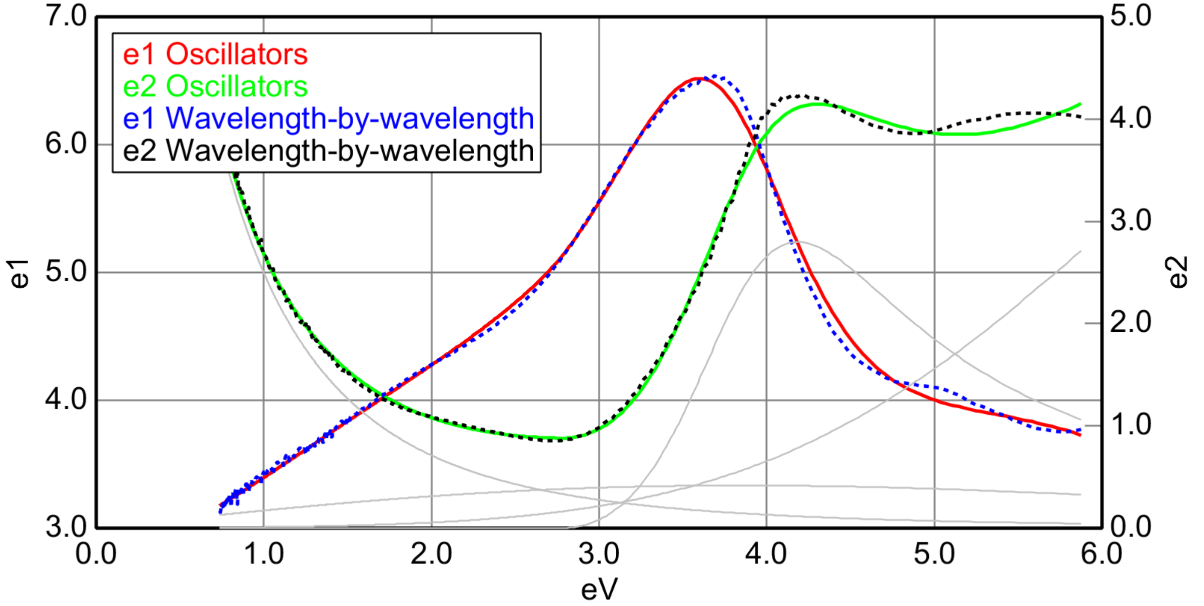
Layer # 1 = NS EMA TLG - Urbach Thickness # 1 = 3.30 nm

Substrate = Silice Eagle XG visir genosc fit

DFs fixed from reference samples

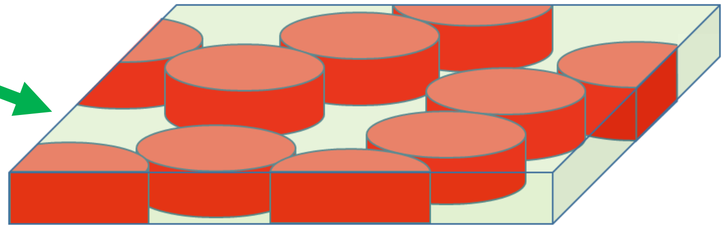
Thickness fixed by XRR measurement

direct calculation of ε_1 and ε_2 + oscillator functions fit



Crystalline $CaVO_3$: sample grown @ 500 °C

Effective Medium (ABEMA) :
- **amorphous $CaVO_3$** (fixed DFs)
- **crystalline $CaVO_3$** DFs fitted by oscilator functions

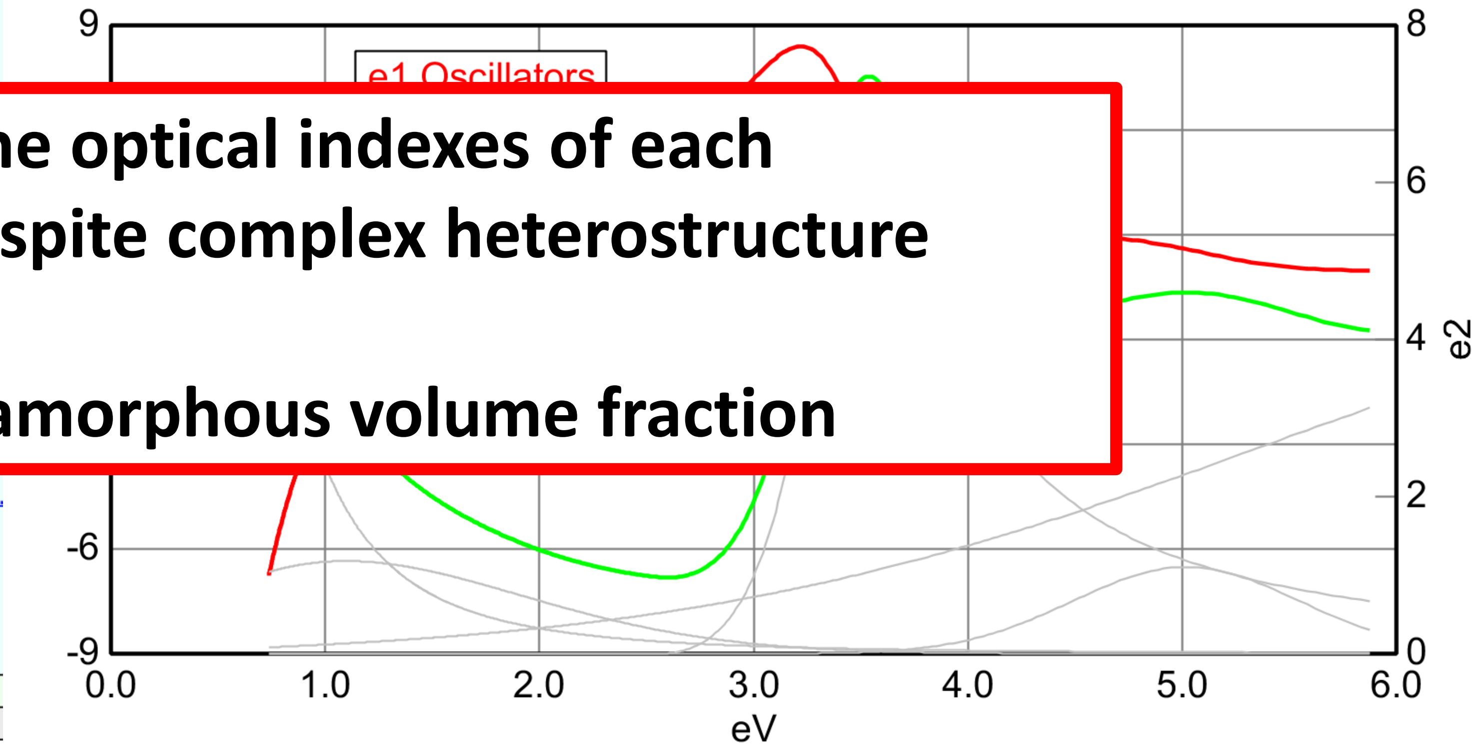


$L_z = 1 \,; L_x/L_y = {}^1/_2$

(Flat cylinders)

Fitted volume fraction *f*
of amorphous $CaVO_3$ = 30 %
➔ consistent with AFM / EBSD !

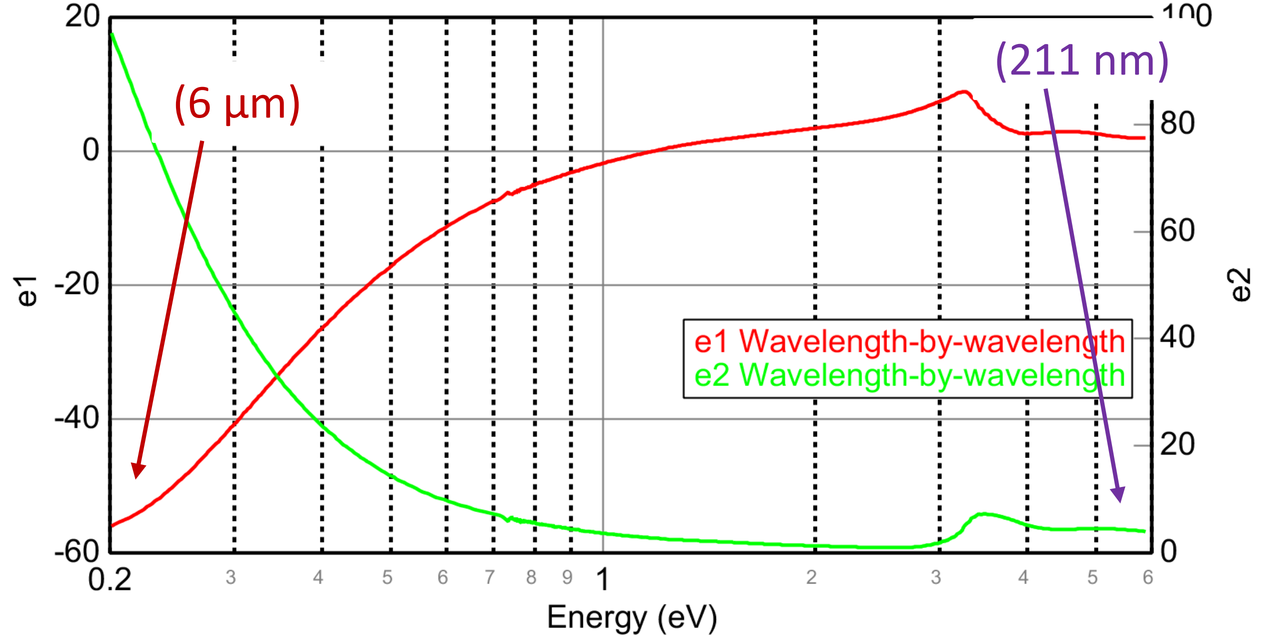
+ Layer # 3 = LAOa Cauchy Thickness # 3 = 5.40 nm
- Layer # 2 = EMA Thickness # 2 = 44.90 nm
  # of Constituents = 2
  - Material 1 = crystalline CVO
    Show Dialog
    - **e1 Components**
      Einf_crystalline CVO = **0.818** (fit)
      UV Pole Amp._crystalline CVO = 0.0
      IR Pole Amp._crystalline CVO = 0.0
    - **e2 Components**
      Oscillator Menu: Add Delete Dele
      Fit Menu: All None Amp. Br. En.
      1: Type = Tauc-Lorentz Amp1_cry
      Br1_crystalline CVO = **0.795** (fi
      2: Type = Drude(RT) Resistivity (
      3: Type = Gaussian Amp3_crystal
      4: Type = Gaussian Amp4_crystal
      5: Type = Gaussian Amp5_crystalline CVO = **5.838524** (fit) Br5_crystalline CVO = 2.
  Material 2 = amorphous CVO
  P_amrophous = **30.2** (fit)
  depolarization (z) = 1.000 depolarization (x-y split) = 0.500
  Euler Angles: Phi = 0.00 Theta = 0.00 Psi = 0.00
  Analysis Mode = Anisotropic Bruggeman
+ Layer # 1 = NS EMA TLG - Urbach Thickness # 1 = 3.30 nm
+ Substrate = Silice Eagle XG visir genosc fit

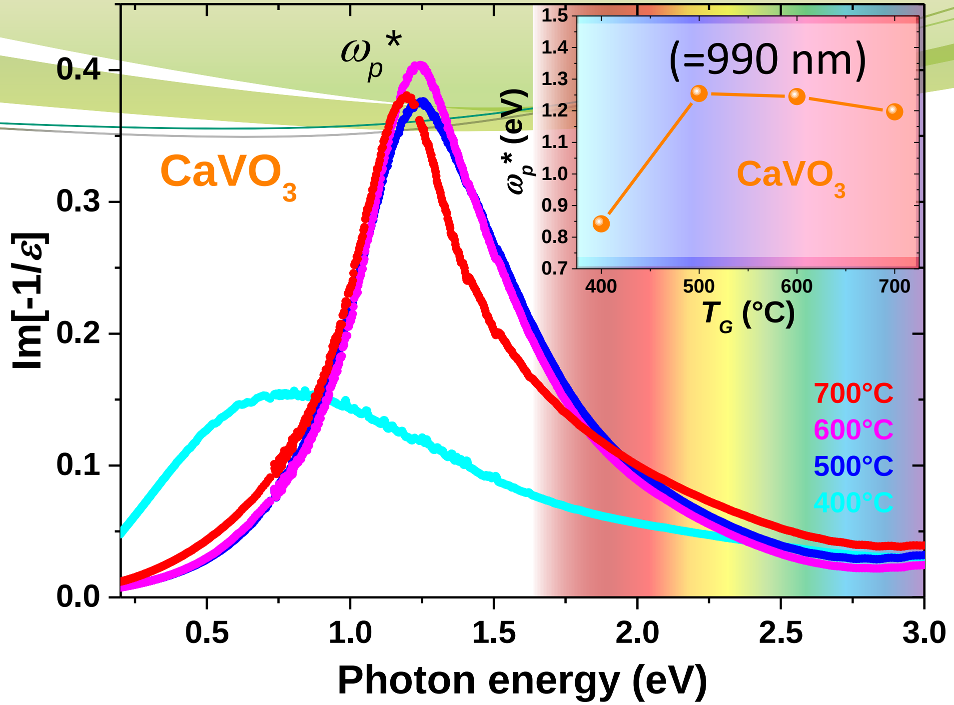


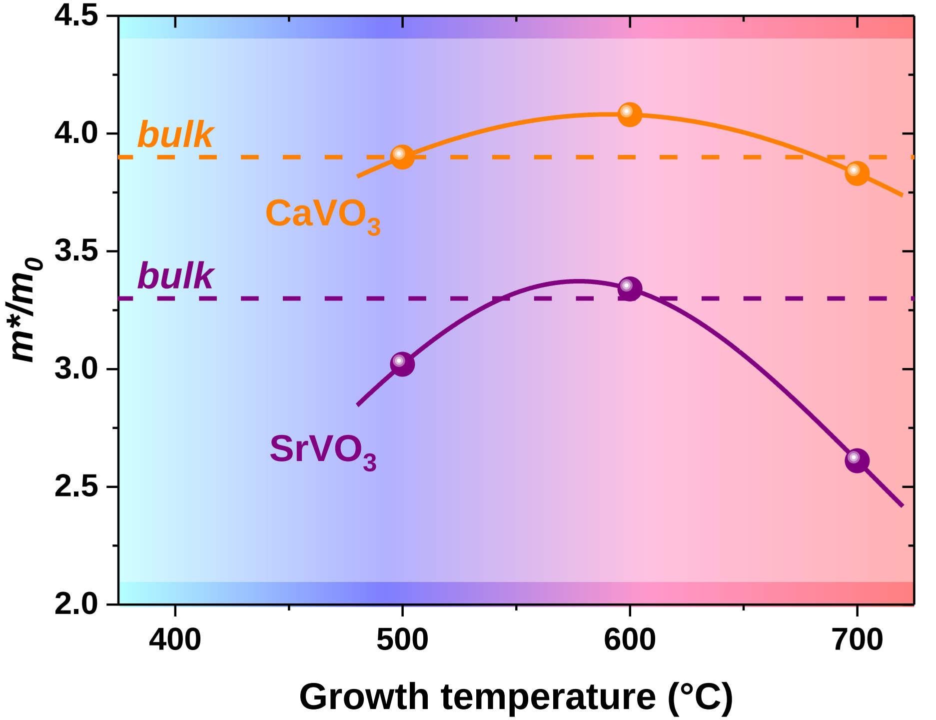
➔ Decorrelate the optical indexes of each component despite complex heterostructure

➔ Quantify the amorphous volume fraction

Infrared properties







- Electronic correlation ➔ **frequency-dependent effective mass m* and scattering time τ** (Extended Drude model) :

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2(\omega)}{\omega^2 + i\omega\gamma(\omega)}$$

- Plasma frequency ω_p = 1.25 eV (990 nm) ➔**IR range**

- m* close to bulk values ➔ **relaxation of strain on NS**

Comparison : optical vs. electrical properties

Crystalline phase (ρ_{DC}^{cryst})

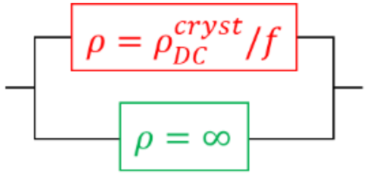
Total DC resistivity (ρ_{DC}) = In-grain + Grain boundary + Network connectivity

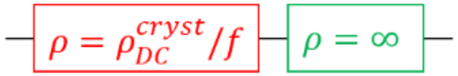
Optical resistivity (ρ_{opt})

Depolarization factor L
Volume fraction f

Effective Medium :

Equivalent circuit :





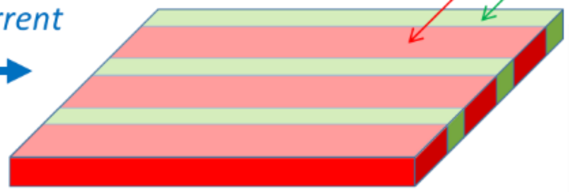
(1) Maximum connectivity :

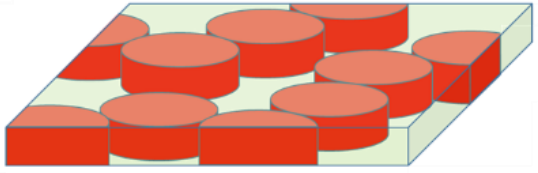
$$\rho_{DC} = \rho_{DC}^{cryst}/f$$

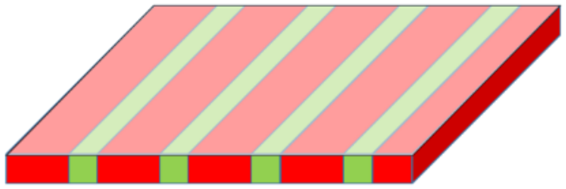
DC current

crystalline (f)

amorphous ($1 - f$)







(2) In general :

$$\rho_{DC}^{cryst} \geq \rho_{opt}$$

Negligible grain boundary

$$\rightarrow \rho_{DC}^{cryst} = \rho_{opt}$$

Maximum connectivity :
$\rho_{DC} = \rho_{DC}^{cryst}/f$

$L = 0$

Intermediate connectivity
(Flat cylinders)

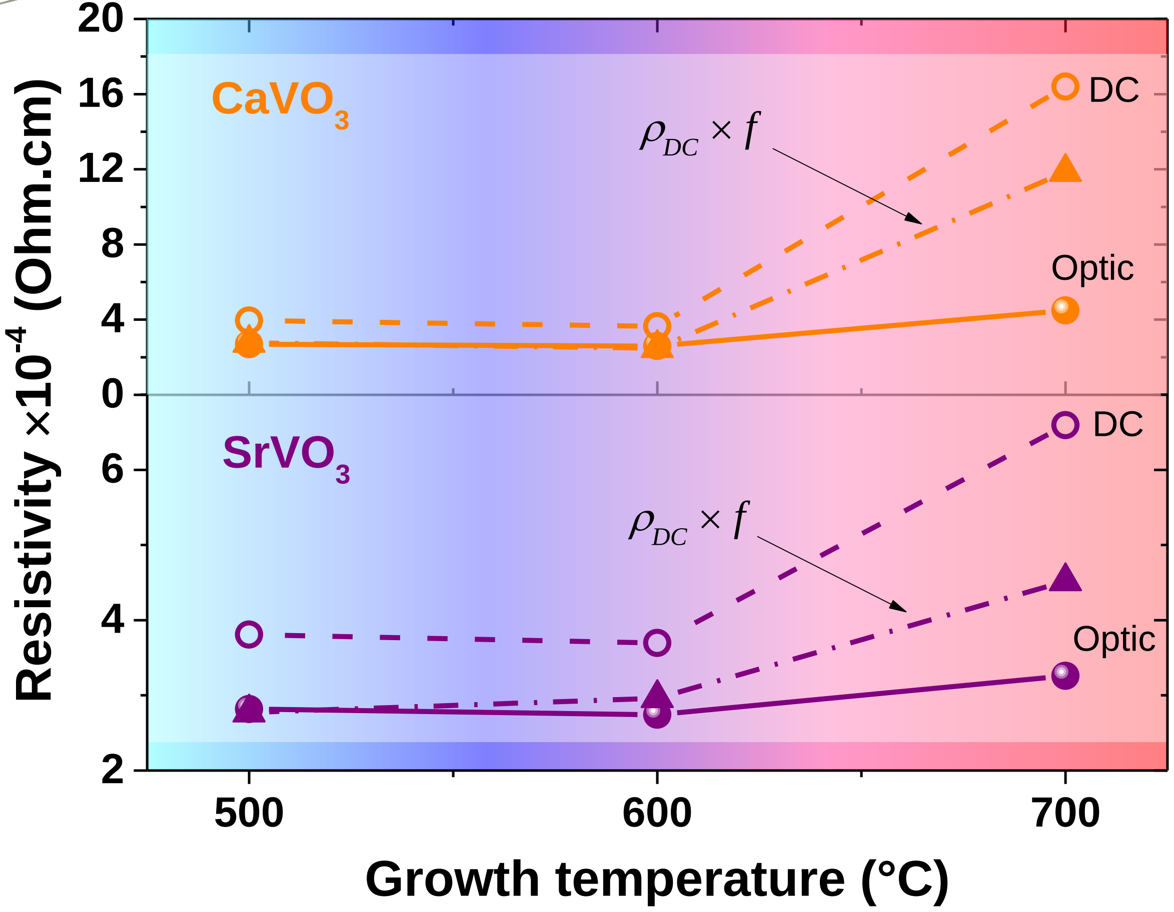
$L = 1/2$

No percolation :
$\rho_{DC} = \infty$

$L = 1$

Vanadates on NS : **$\rho_{DC} = \rho_{opt}/f$ ➔ Maximum connectivity (1) + Negligible grain boundary (2) !**

Comparison : optical vs. electrical properties



- $\rho_{DC} = \rho_{opt}/f$ @ 500 and 600°C

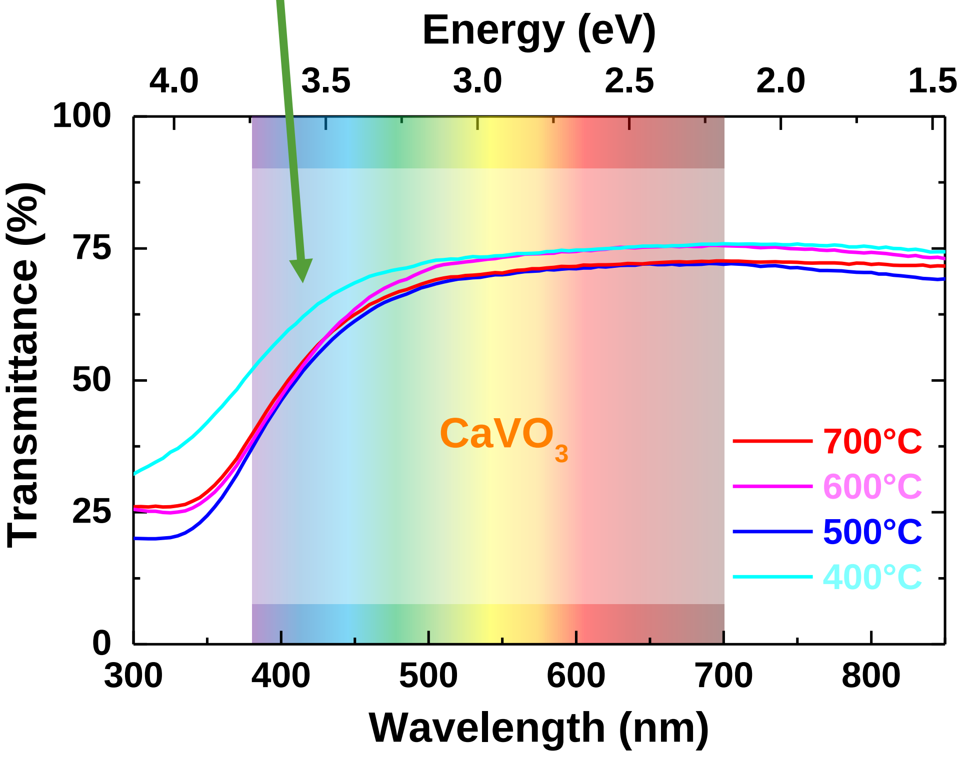
➔ **Maximum connectivity + Negligible grain boundary**

- @ 700°C :
  - ρ_{opt} increase ➔ **in-grain degradation**
  - $\rho_{DC} > \rho_{opt}/f$ ➔ **grain boundaries appear**

Performance as a transparent conductor

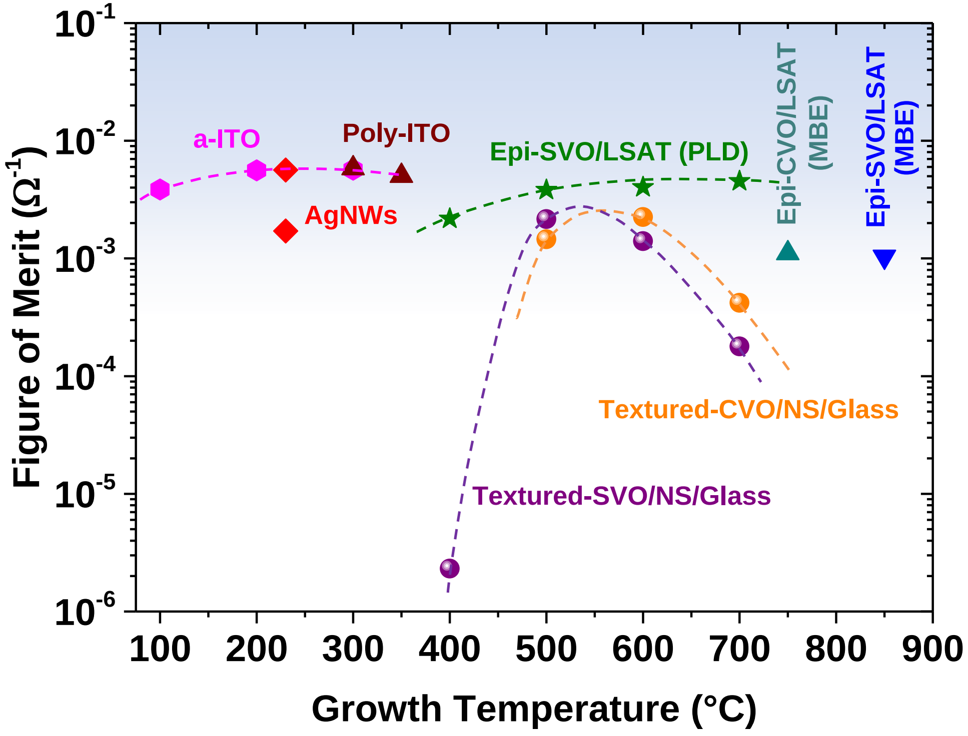
Visible : Transparency = 75 %

Amorphous phase is more transparent
➔ increase amorphous proportion ?



Haacke figure of merit = $T^{10}/R_{\square}$

➔ as good as epitaxial vanadates or ITO
➔ reduced growth temperature



Conclusions

- Successfull growth of vanadates on Glass substrate thanks to NS

- Performances : as good as ITO or epitaxial vanadates

- Spectroscopic Ellipsometry with EMA :
  - ➢ optical indexes of crystalline and amorphous phase
  - ➢ proportion of amorphous phase (↔ NS coverage)

- Optical-DC comparison with EMA :
  - ➢ Good connectivity
  - ➢ Negligible grain boundary

- NS coverage = lever to tune properties :

(e.g. : increase amorphous proportion, patterning)