Thickness effect on vanadate TCO integrated on glass substrates using 2D nanosheets as a template

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Vanadate Perovskite as a new TCO

ARTICLES
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Correlated metals as transparent conductors

Lei Zhang[1,2], Yuanjun Zhou[3], Lu Guo[1,2†], Weiwei Zhao[4], Anna Barnes[5,6], Hai-Tian Zhang[1,2], Craig Eaton[1,2], Yuanxia Zheng[1,2], Matthew Brahlek[1,2], Hamna F. Haneef[5,6], Nikolas J. Podraza[5,6], Moses H. W. Chan[4], Venkatraman Gopalan[1], Karin M. Rabe[3] and Roman Engel-Herbert[1,2*]

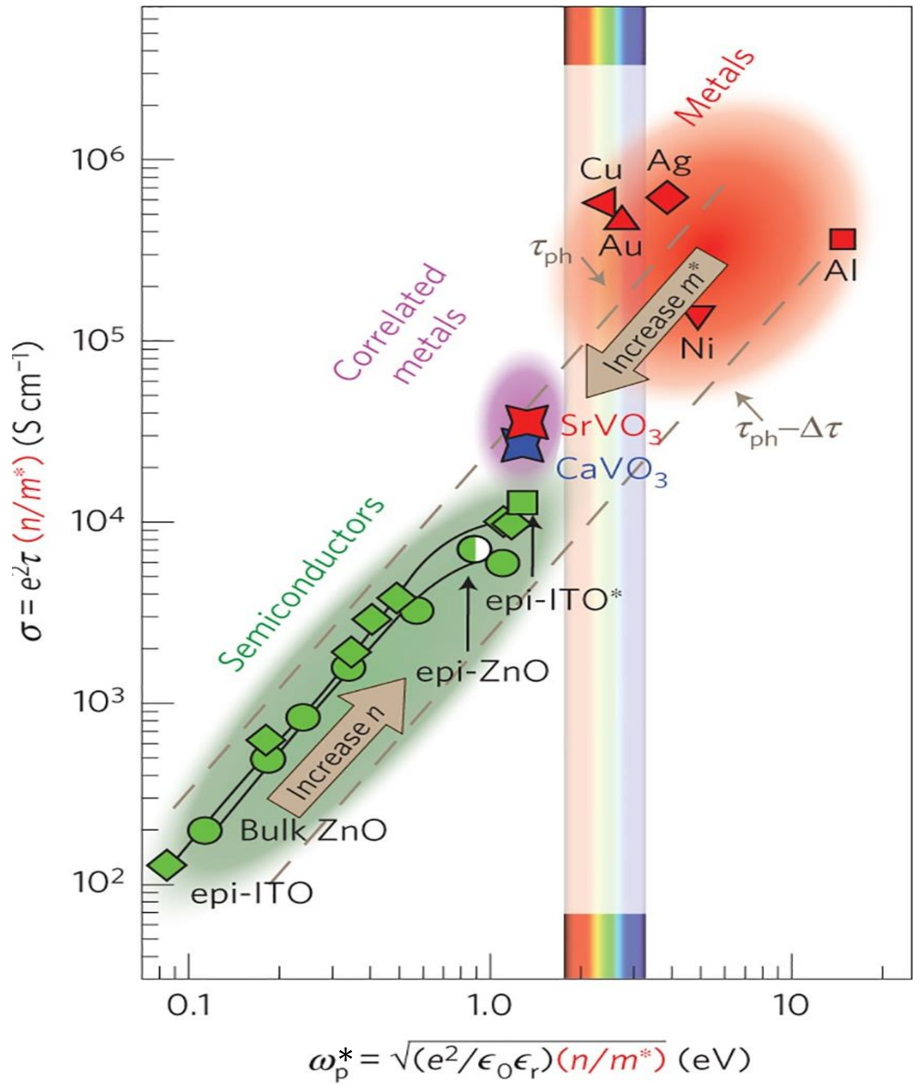
The fundamental challenge for designing transparent conductors used in photovoltaics, displays and solid-state lighting is the ideal combination of high optical transparency and high electrical conductivity. Satisfying these competing demands is commonly achieved by increasing carrier concentration in a wide-bandgap semiconductor with low effective carrier mass through heavy doping, as in the case of tin-doped indium oxide (ITO). Here, an alternative design strategy for identifying high-conductivity, high-transparency metals is proposed, which relies on strong electron–electron interactions resulting in an enhancement in the carrier effective mass. This approach is experimentally verified using the correlated metals $SrVO_3$ and $CaVO_3$, which, despite their high carrier concentration ($>2.2 \times 10^{22}$ cm^{-3}), have low screened plasma energies (<1.33 eV), and demonstrate excellent performance when benchmarked against ITO. A method is outlined to rapidly identify other candidates among correlated metals, and strategies are proposed to further enhance their performance, thereby opening up new avenues to develop transparent conductors.

The growing demand of high-performance and cost-effective material solutions for transparent conductors has been fuelled by the rapidly growing markets of display technologies, photovoltaics, smart windows and solid-state lighting industries.

by $\Delta\tau$ due to an enhanced ionized and neutral impurity scattering from the high dopant concentration marks a second limitation to this design strategy.

As the screened plasma energy is much below the visible range

Why $SrVO_3$ and $CaVO_3$ can substitute ITO?



TCO

High electrical conductivity

$$\sigma = e\mu n = e^2\tau\frac{n}{m^*}$$

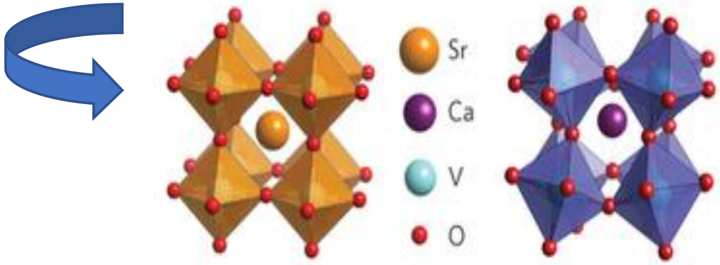
High transparency in the visible range

$$\omega_p^* = \frac{e}{\sqrt{\varepsilon_0\varepsilon_r}}\sqrt{\frac{n}{m^*}}$$

ITO

- Mostly used in industry

Low abundance of In in Earth's crust (0.1 ppm)



Vanadate TCO as new strategic TCO

Indium-free material…

He, H.et al. (2020). Perovskite oxides as transparent semiconductors: a review. *Nano Convergence*, *7*(1), 1-10.
Zhang, L.,et al. (2016). Correlated metals as transparent conductors. *Nature materials*, *15*(2), 204-210.

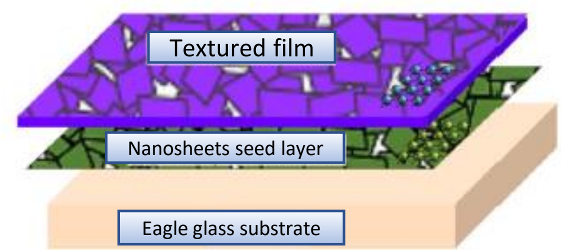
Vanadate TCO on single crystal substrates

- Costly materials
- Limited substrate size

Vanadate TCO on non adapted substrate

Vanadate TCO: Nanosheets

- Crystallized and textured films at 500°C
- Enhanced conductivity
- High transparency in the Visible range



Aim

Study the thickness effect on vanadate TCO integrated on glass substrates using 2D nanosheets as a template

Boileau et al. (2022). *Advanced Functional Materials*, *32*(5), 2108047.

Outline

- Substrate preparation
- $SrVO_3$ ($CaVO_3$) film
  - Deposition
  - Macroscopic structural and electrical properties
  - Microscopic electrical properties
  - Optical properties
- Conclusion and perspectives

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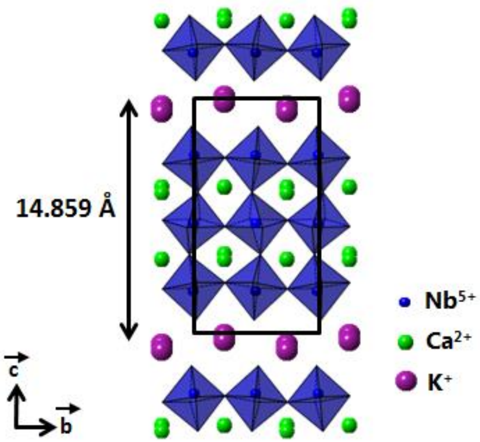
Deposition of CNO nanosheets on glass substrates

CNO preparation

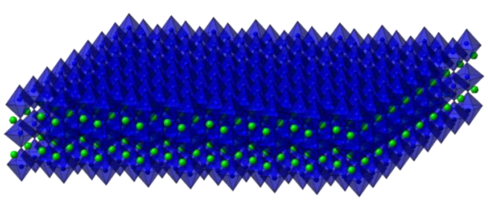
Layered perovskite Dion-Jacobson phase

$KCa_2Nb_3O_{10}$ (KCN)

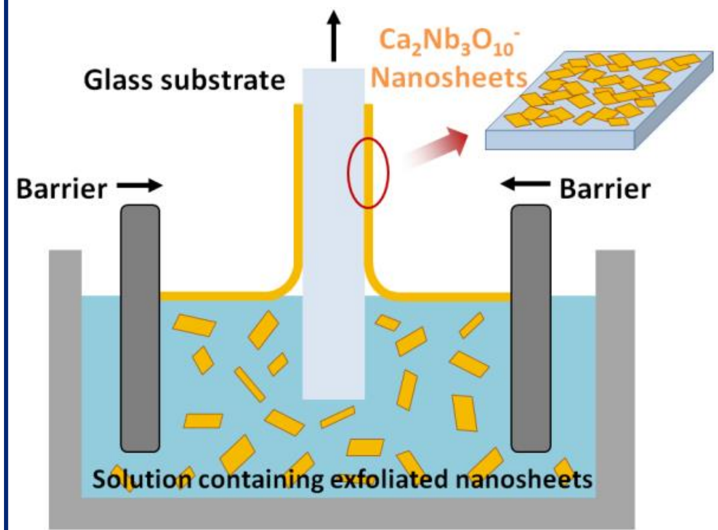


After exfoliation

$Ca_2Nb_3O_{10}^-$ nanosheet

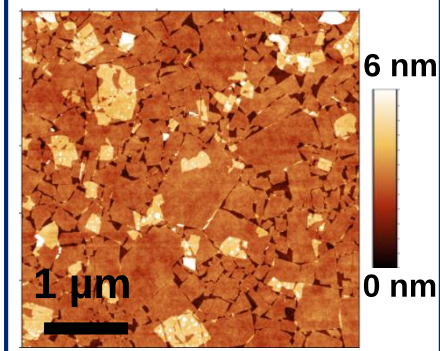


CNO deposition



Langmuir- Blodgett

AFM



covering rate ~ 80%

- ✓ Successful synthesis and deposition of CNO
- ✓ Good coverage of the glass substrate

Collaboration V. Demange

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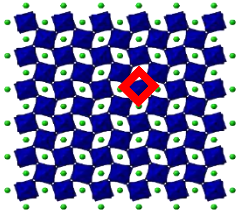
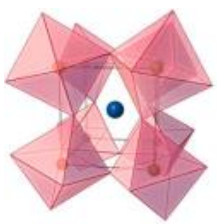
Deposition of $SrVO_3$ ($CaVO_3$) thin films

CNO an adapted template



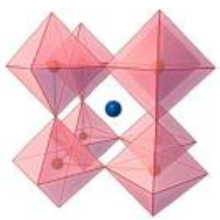
In plane view of $Ca_2Nb_3O_{10}^-$ nanosheet

a_{NS} ~ 3.85 Å



$CaVO_3$ Orthorhombic ($Pbnm$)

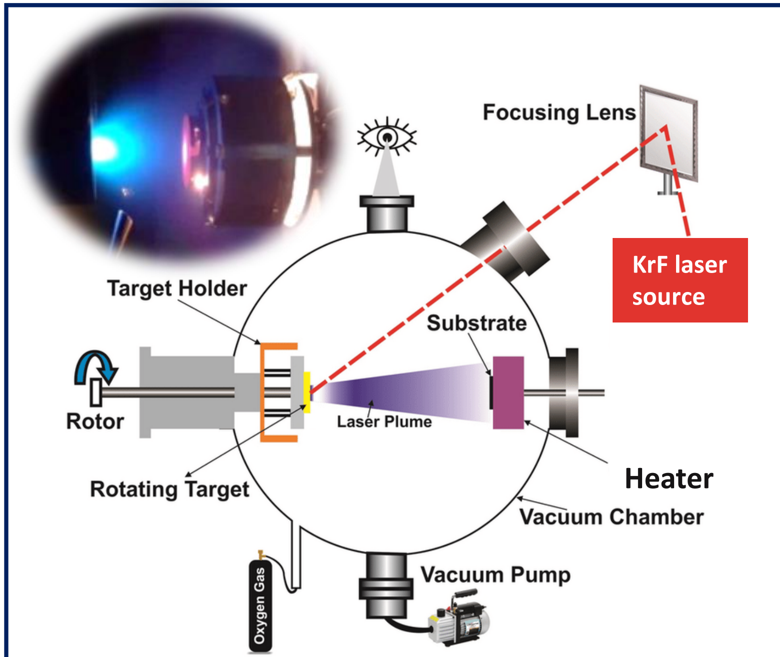
a_{pc} = 3.77 Å Misfit = -2,17%



$SrVO_3$ Cubic ($Pm\overline{3}m$)

a = 3.84 Å Misfit = -0,34%

Pulsed Laser deposition (PLD)



- Temperature = 500 °C
- Pressure = 1×10^{-6} mbar
- Film Thickness = 10, 20 and 40 nm

- ✓ Successful deposition of the films
- ✓ Thickness in good agreement with the desired ones (XRR)

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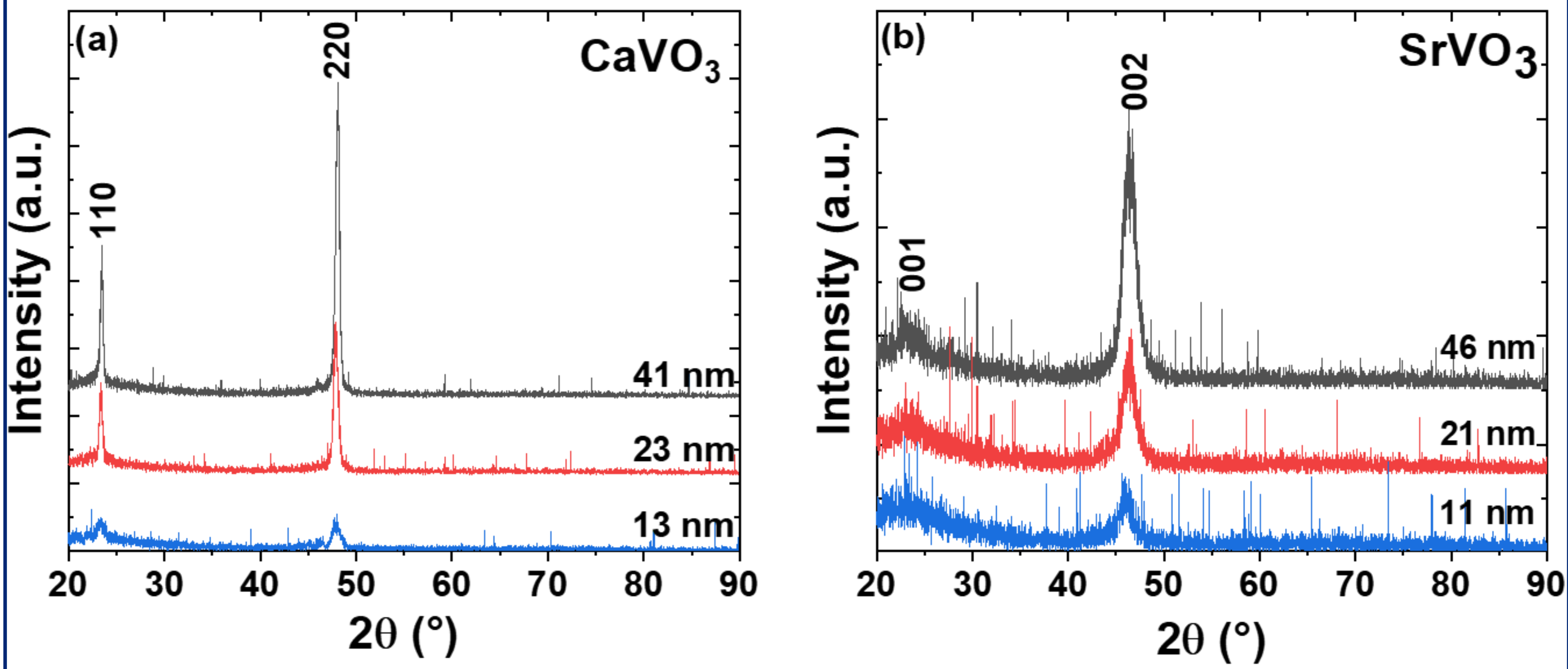
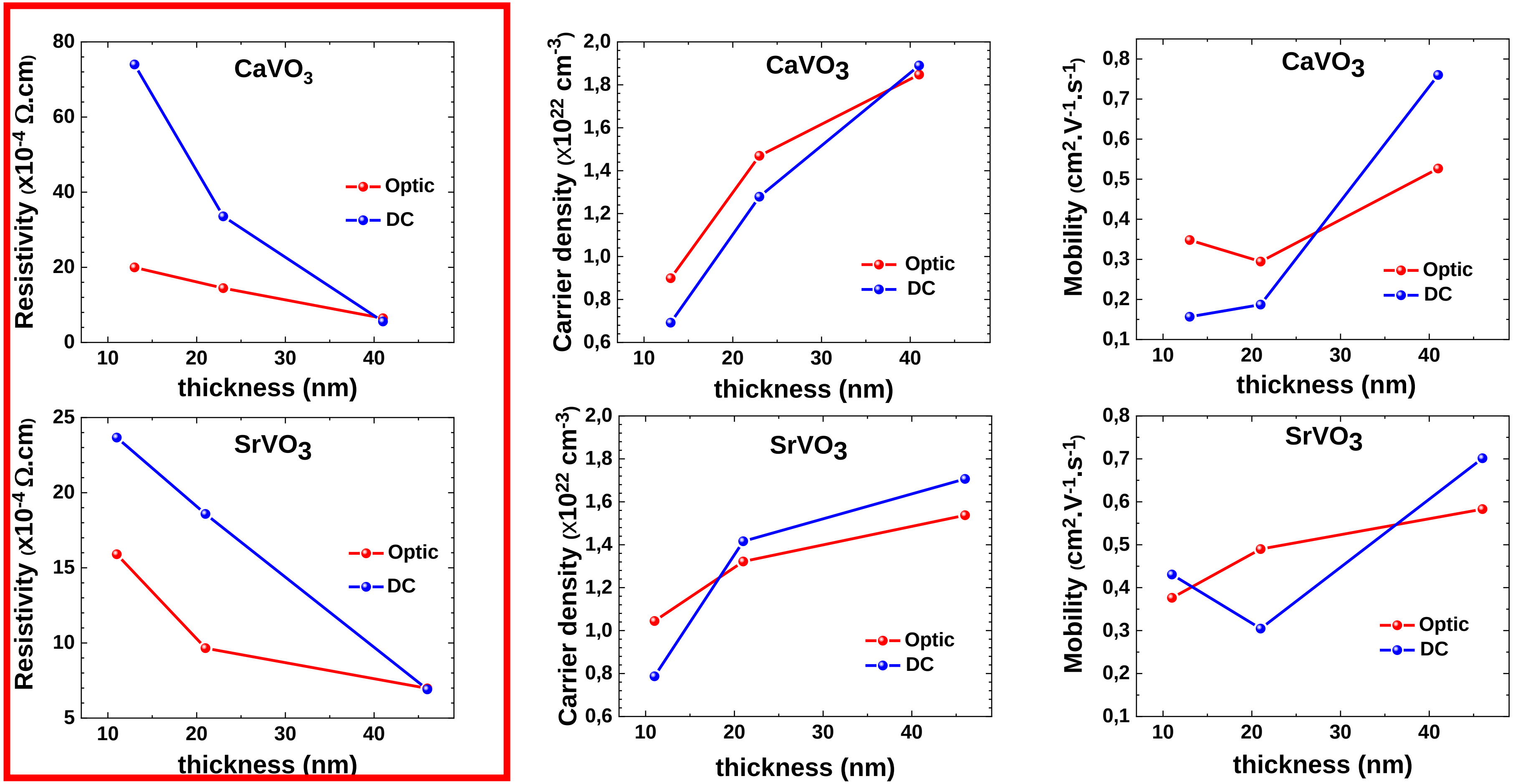
Structural properties of the films

XRD



- ✓ Crystallized and textured CVO and SVO films
- ✓ Increase of peaks intensity with thickness

Optical properties by ellipsometry vs transport DC



- ✓ **Difference between optic and DC resistivity for 10 and 20 nm films**
- ✓ **Conductivity, carrier density and mobility: decrease as the film is thinner.**

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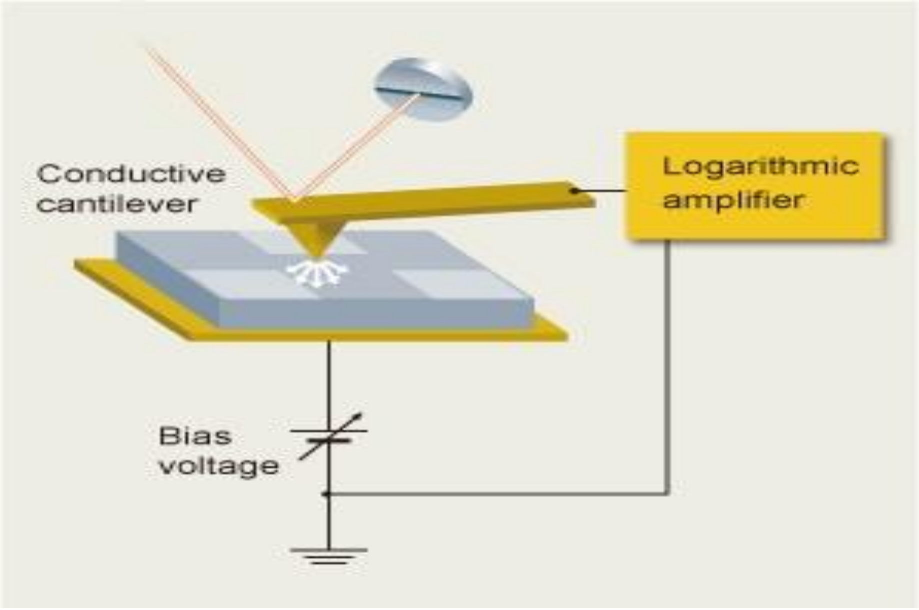
Microscopic electrical properties

Scanning Spreading Resistance Microscopy (SSRM)

SSRM Principle

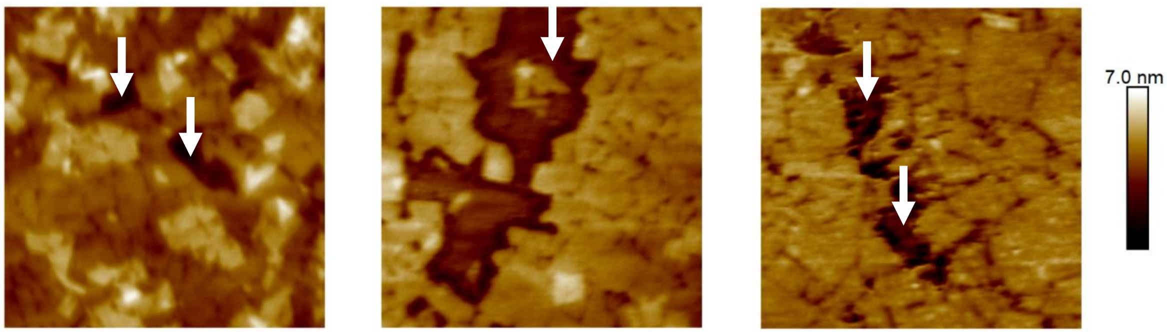


- ✓ **Electrical contact AFM mode**
- ✓ **Bias voltage applied to the sample**
- ✓ **Current is collected and the resistance is measured using a logarithmic amplifier**

Microscopic electrical properties

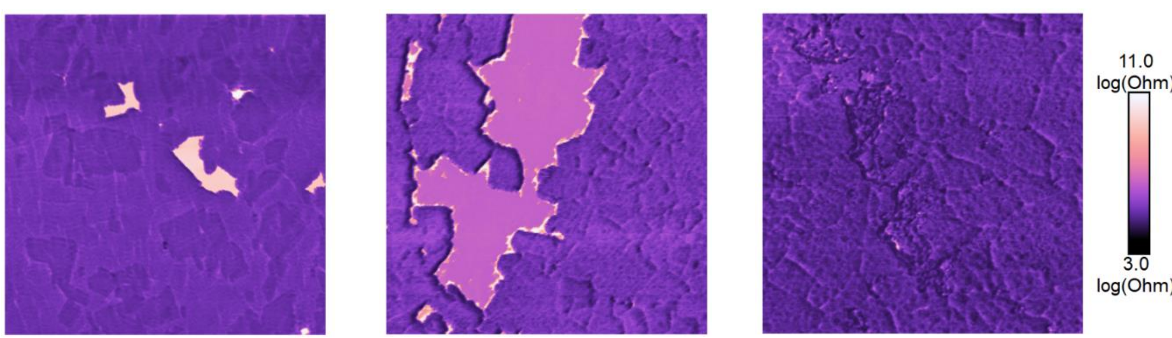
Scanning Spreading Resistance Microscopy (SSRM)

Topography

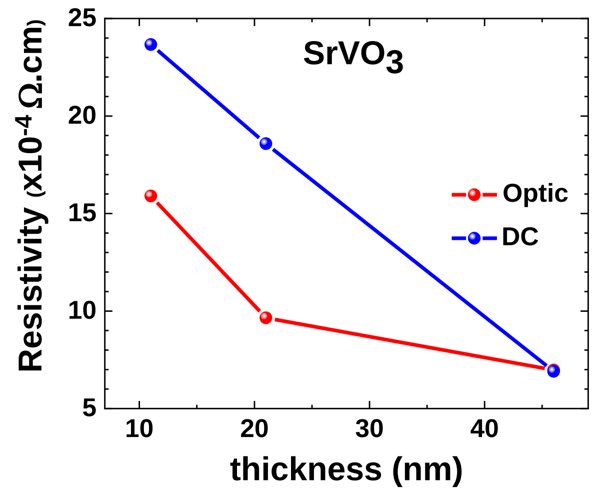


11 nm | 21 nm | 46 nm

Log (resistance)



11 nm | 21 nm | 46 nm

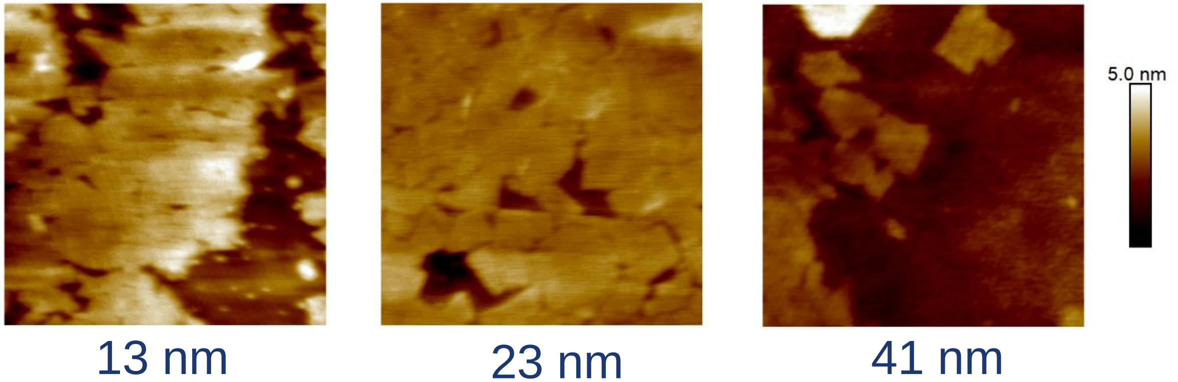


- ✓ 46 nm film: covered and uncovered areas present same resistance
- ✓ 21 and 11 nm: uncovered areas are more resistive

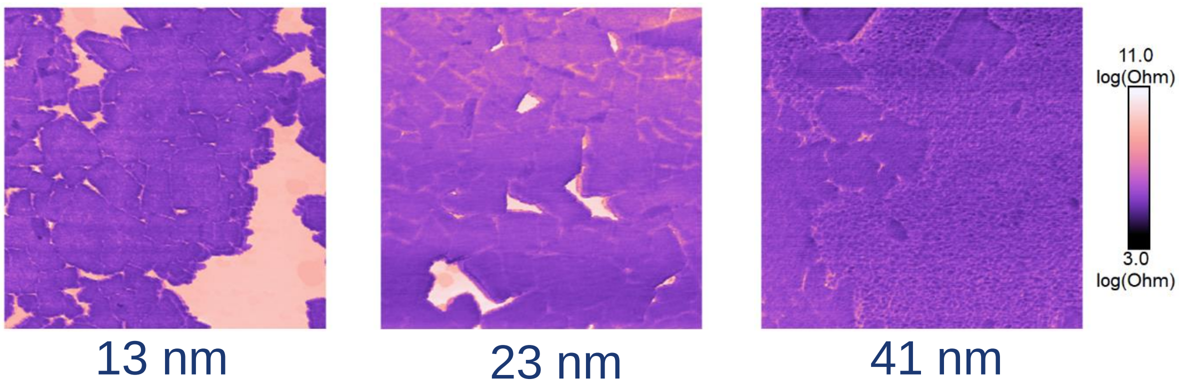
Microscopic electrical properties

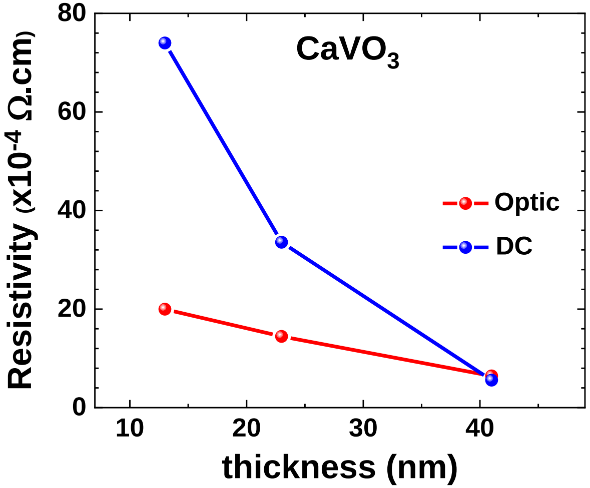
Scanning Spreading Resistance Microscopy (SSRM)

Topography



Log (resistance)





- ✓ 41 nm film: covered and uncovered areas present same resistance
- ✓ 23 and 13 nm: uncovered areas are more resistive

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Optical properties by ellipsometry

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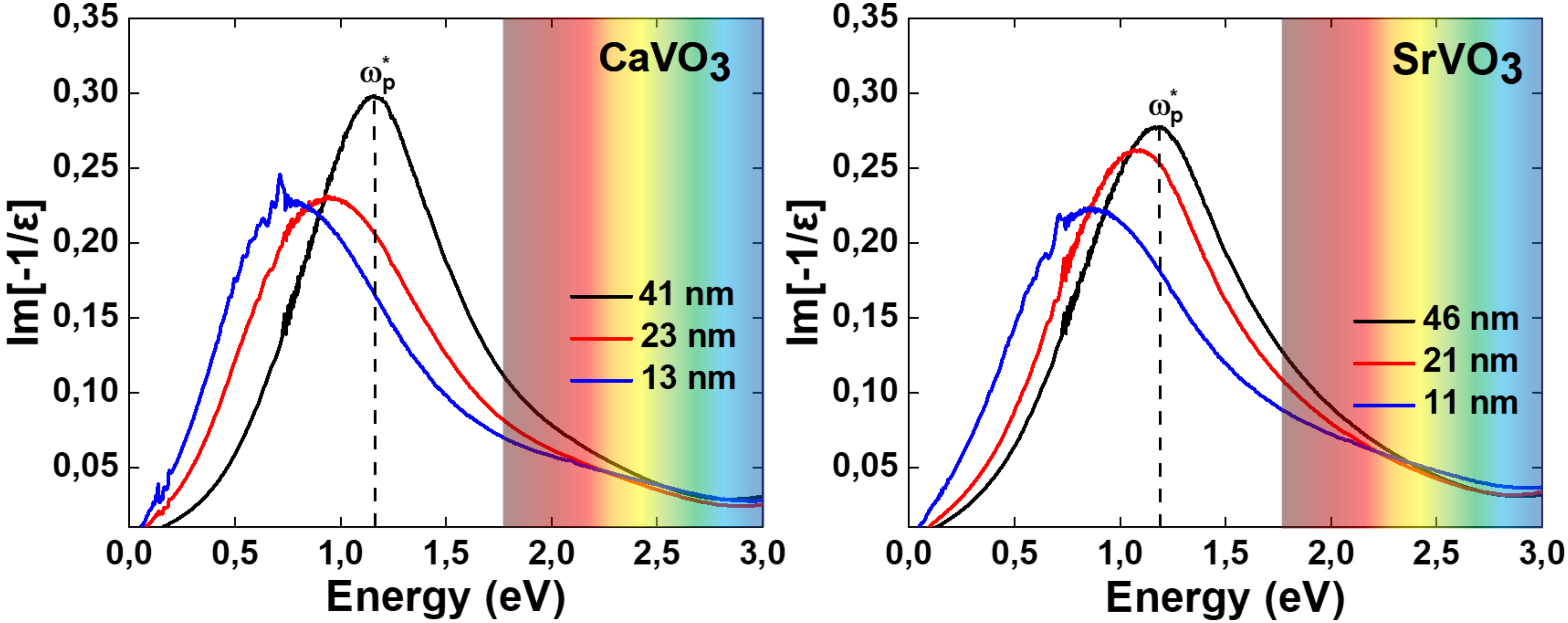
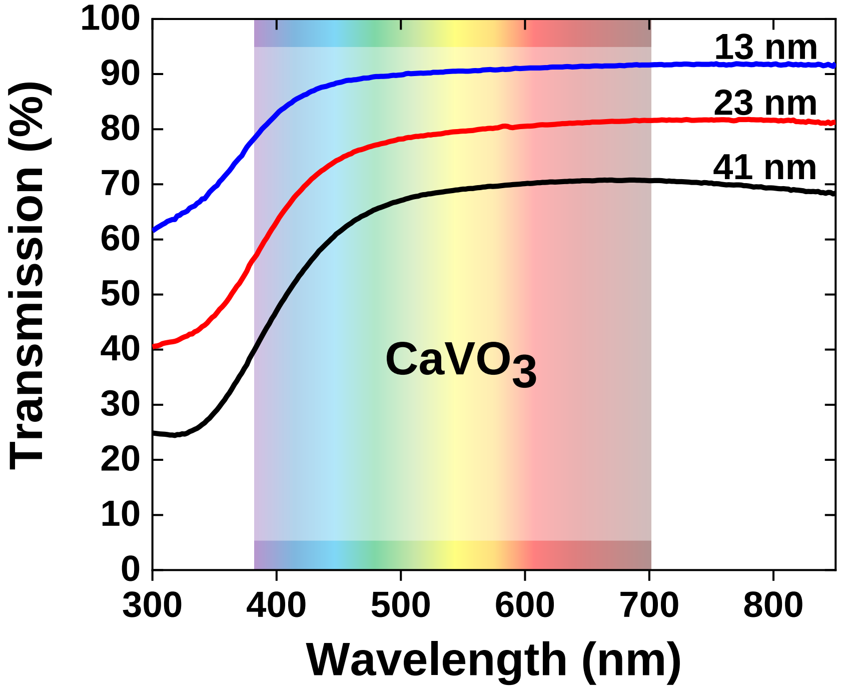
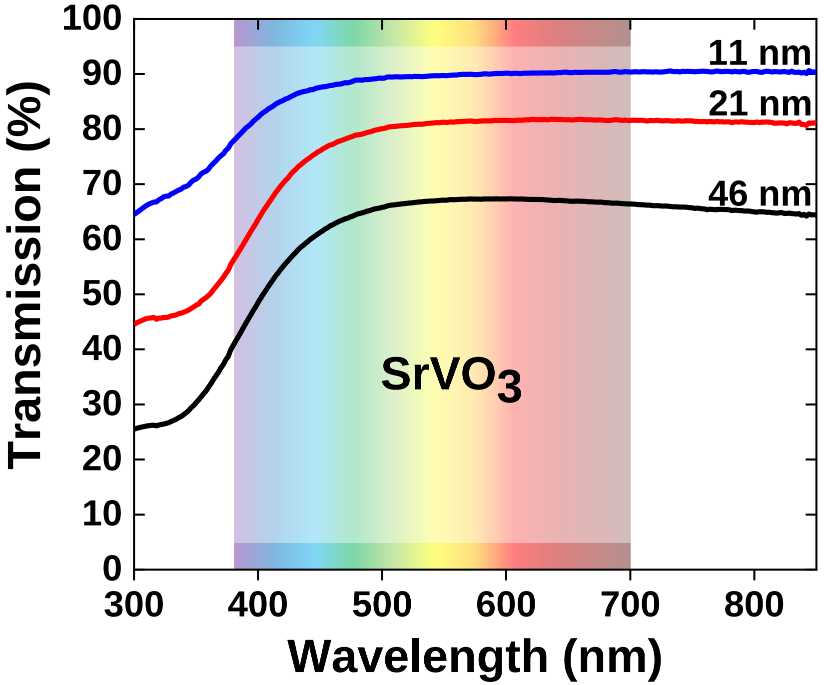
Plasma frequency



- ✓ Screened plasma frequency is below the visible range.
- ✓ Screened plasma frequency shifts to the infrared region as the thickness decreases.

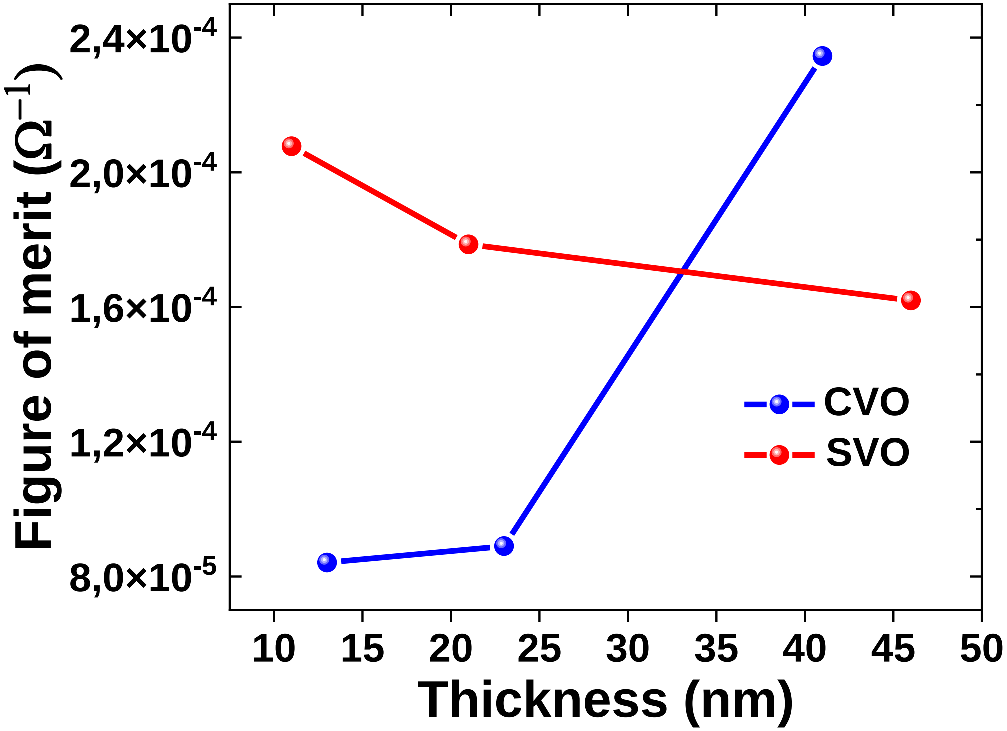
Optical properties by Transmission





- ✓ Transparency of the films in the visible range.
- ✓ Comparable transmission with that of films grown on suitable substrates.
- ✓ Increase of transmission as the thickness decreases.

Haacke figure of merit (FOM)



$$\phi_{TC} = \frac{T^{10}}{R_S}$$

- ✓ **For SVO, FOM increases when the thickness decreases.**
- ✓ **For CVO, FOM decreases when the thickness decreases, due to the increase of resistance**

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Conclusion

- Crystallized and textured vanadate films
- Good electrical properties: decreasing with thickness
- Excellent transmission in the visible range: increasing with the thickness decrease

Perspectives

- Further development of the microscopic electrical measurements (SSRM)
- Control of the covering rate of the nanosheets (LB, …)
- Large surface deposition (PLD …)

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