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Development of Granular Metals for High Voltage Applications

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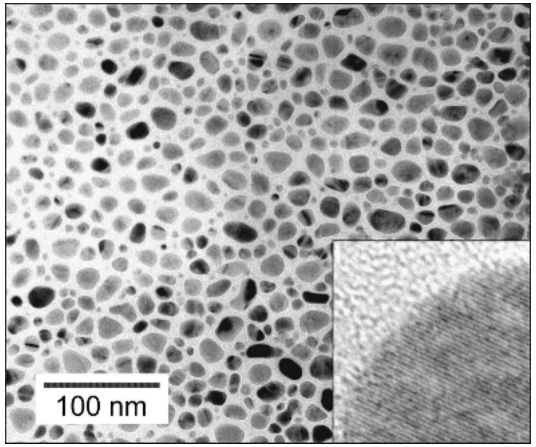
Outline

What are granular metals?

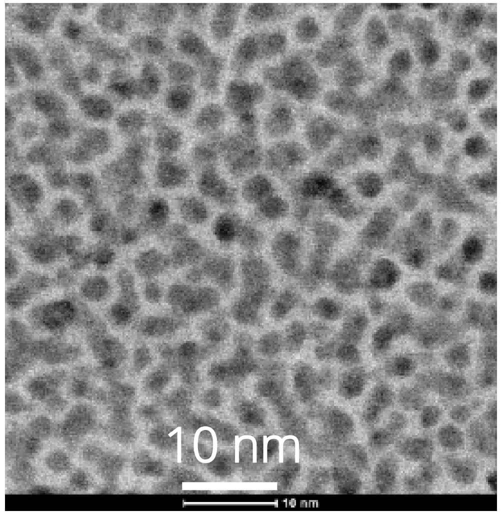
How does their nanostructure influence transport properties?

How can we optimize this nanostructure for high voltage applications?

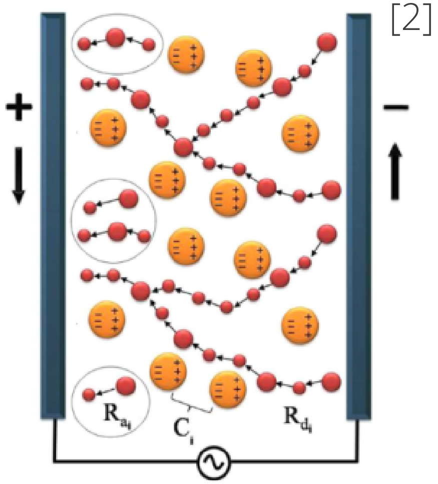
Summary



Cobalt/yttria-stabilized ZrO_2 (Co/YSZ) [1]



Pd/YSZ (Sandia)

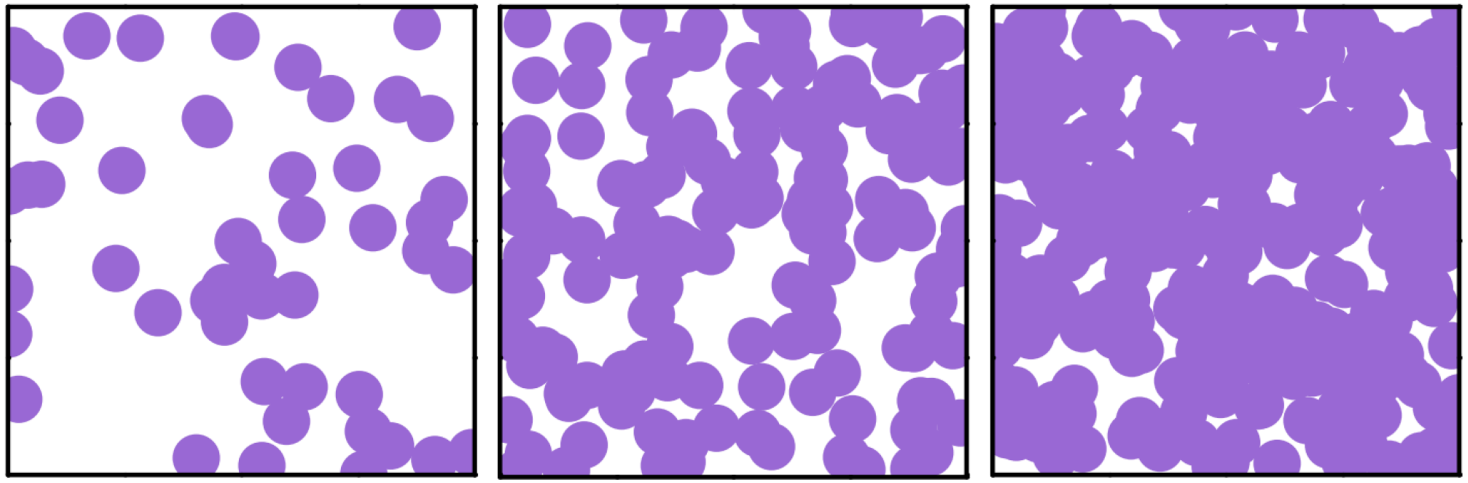


[1] Hattnik *et al.*, PRB 2003. [2] Bakkali *et al.* J. Scientific Reports (2016)

Granular metals comprise metal islands embedded in an insulating matrix

Dielectric | Percolation threshold | Metal

$\phi < \phi_c$ | $\phi \approx \phi_c$ | $\phi > \phi_c$



Common metals

Ag, Au, Ni, Pd, Co, Fe

Common insulators

SiO_2, Al_2O_3, yttria-stabilized zirconia (YSZ)

$$\sigma \propto \exp\left(-1.41 \frac{D}{\xi \varphi^{\frac{1}{3}}}\right)$$

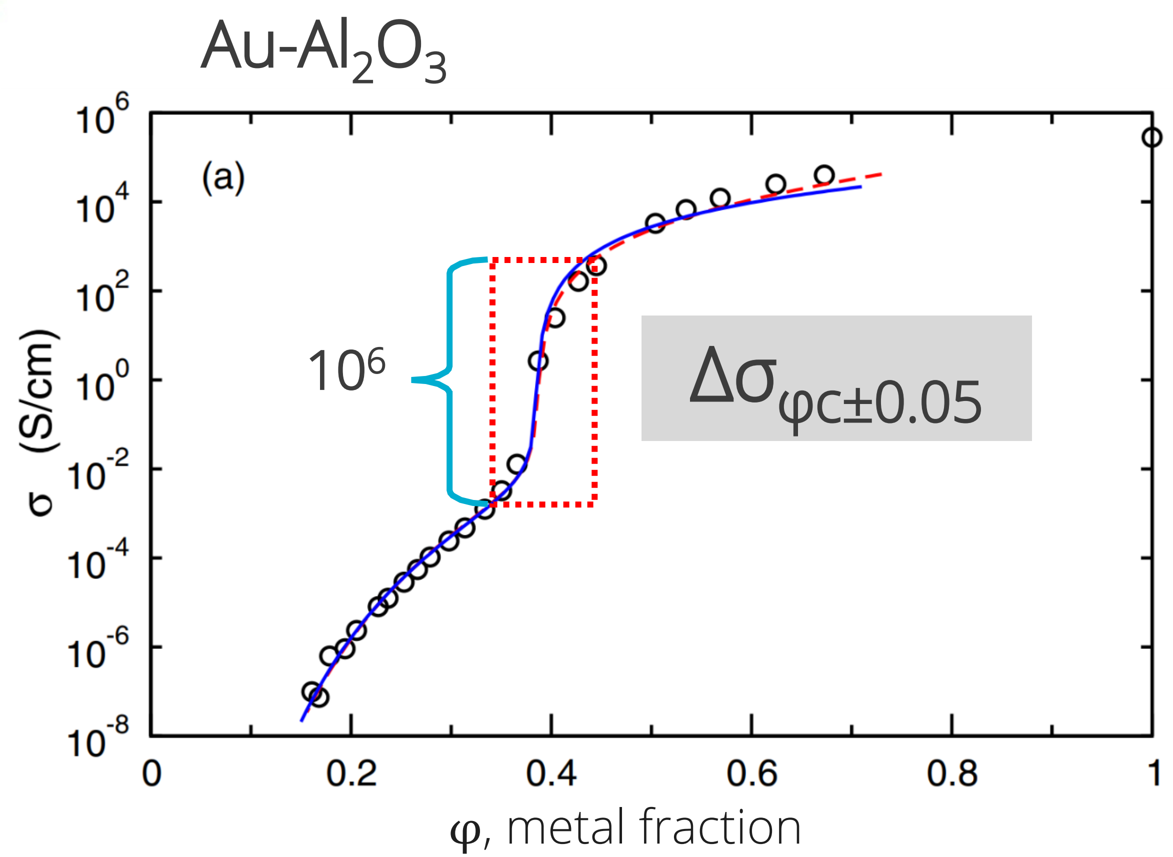
$$\cong \; {}_0 \; (\quad - \quad)^2$$

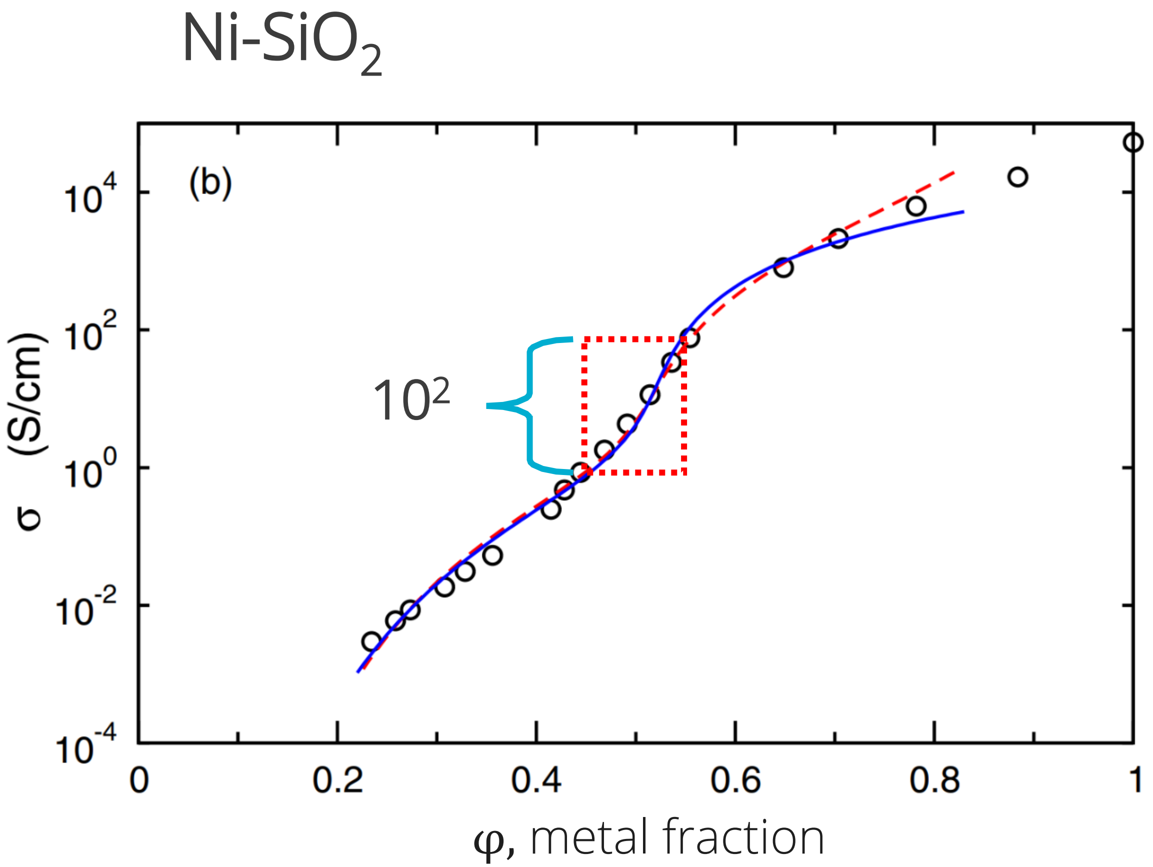
Island diameter, *D*, ~ 1—10 nm

Tunneling decay length, *ξ*, ~ 0.1 – 1 nm

Grimaldi, Phys. Rev. B **89**, 214201 (2014)

Similar granular metal systems exhibit large variances in dc conductivity





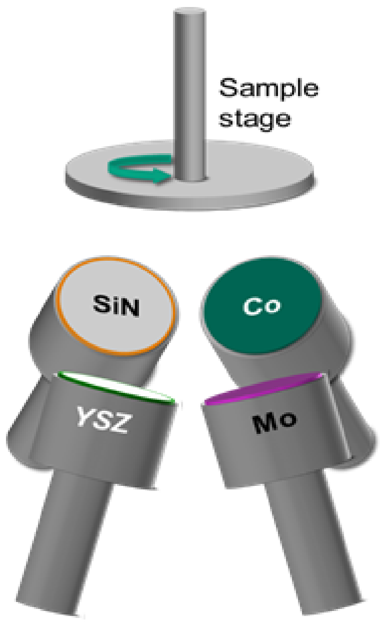
Data: Abeles *et al*. Adv. in Phys. **24**, 407 (1975); *Figures*: Grimaldi, Phys. Rev. B **89**, 214201 (2014).

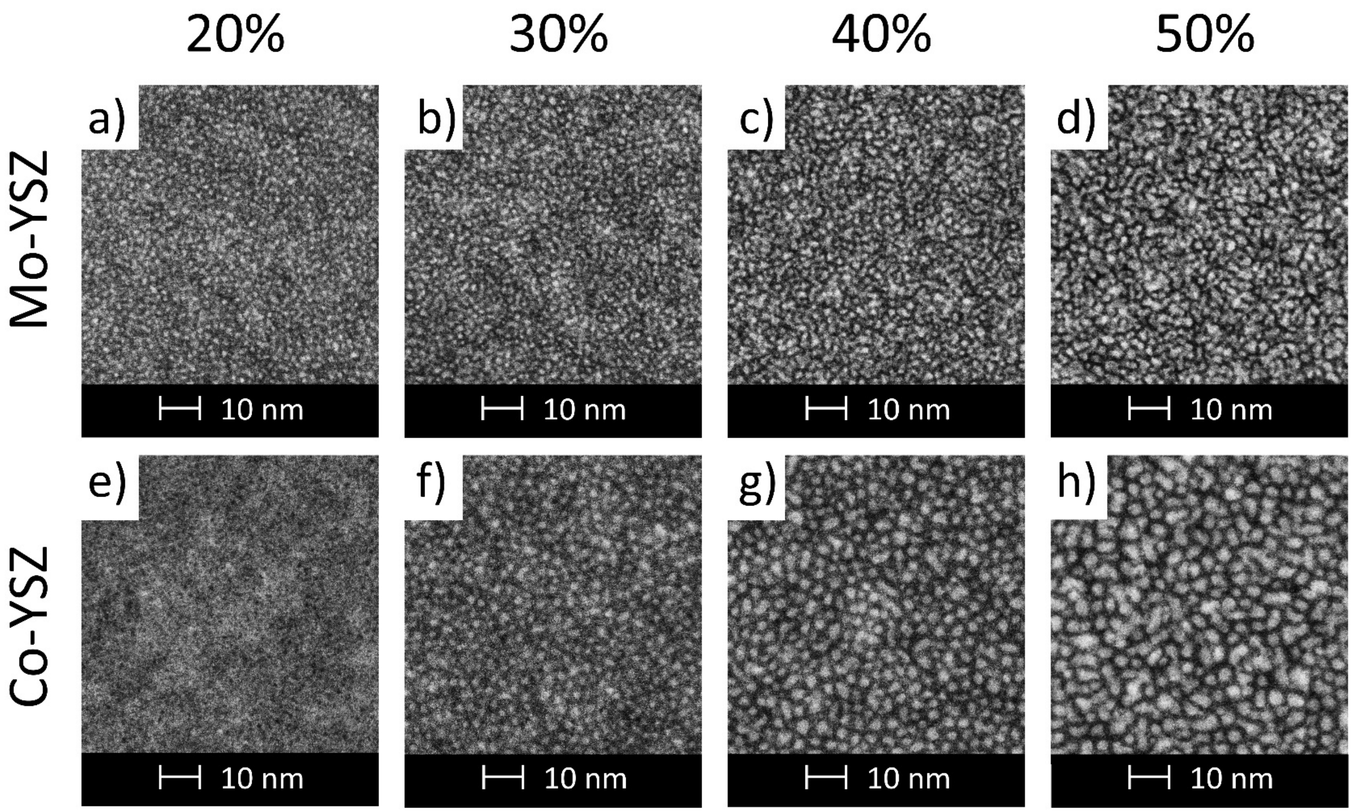
Optimized rf sputtering geometry, power, and pressure to grow well -controlled granular metal films

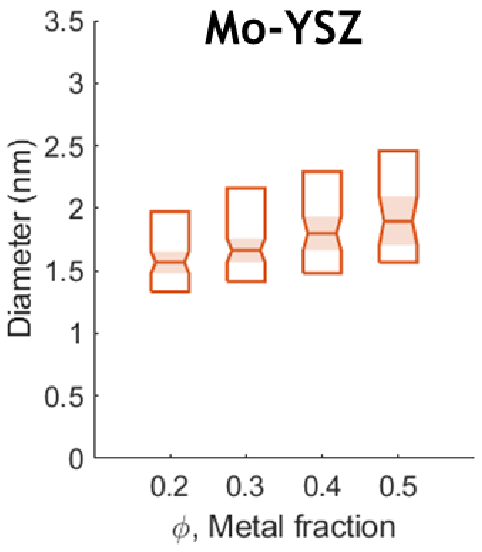
Vary metal/ceramic ratio by adjusting the rf power of the metal while keeping insulator power constant.

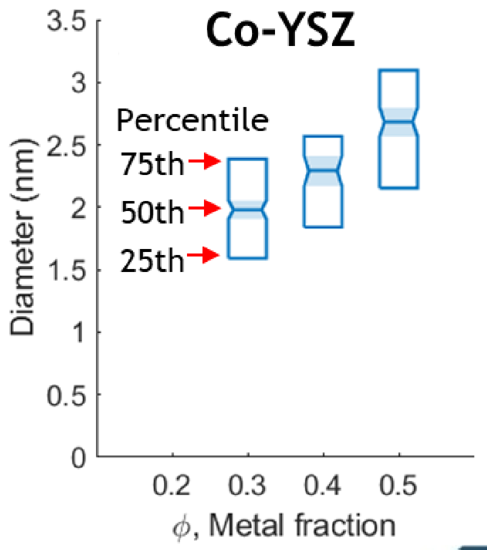
Lower rf power (<100 W) minimizes in-situ annealing during deposition.

5 mTorr argon



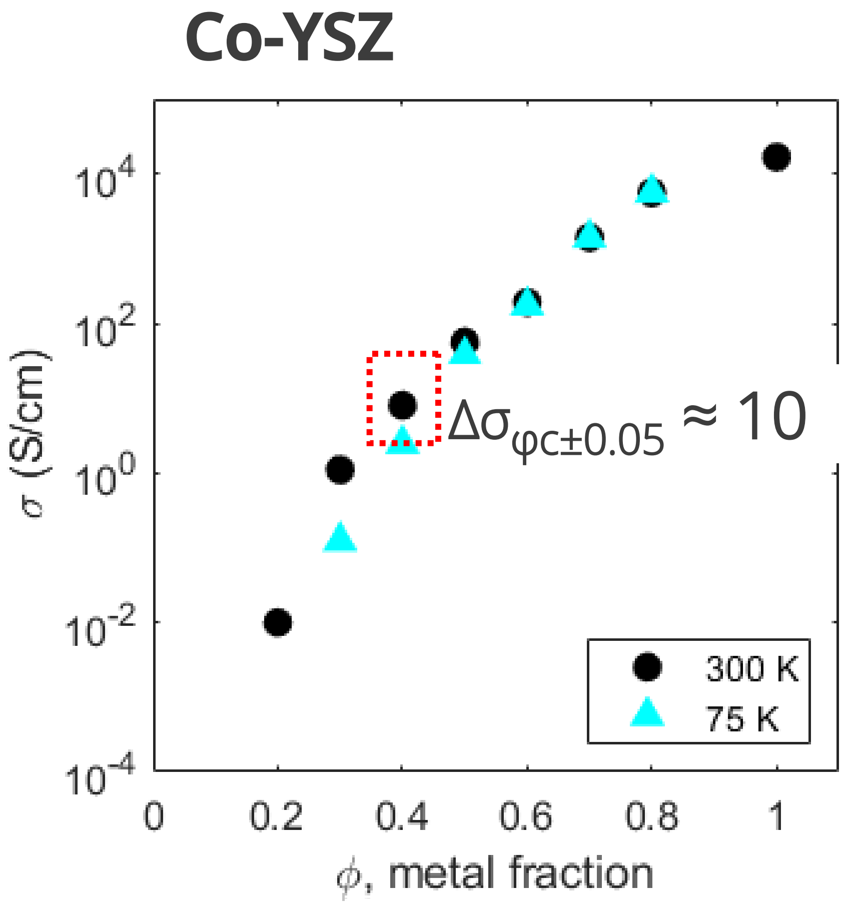


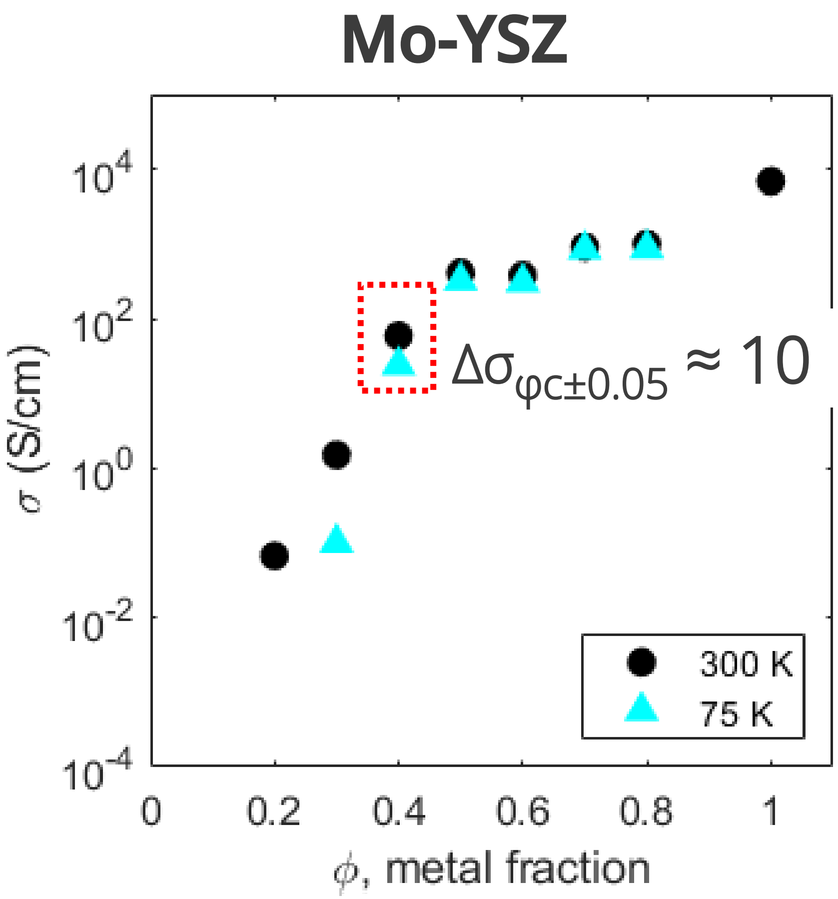




S.J. Gilbert *et al*., J. Phys. Condens. Matter **34**, 204007 (2022).

Conductivity curves for Co-YSZ and Mo-YSZ are characteristic of GMs





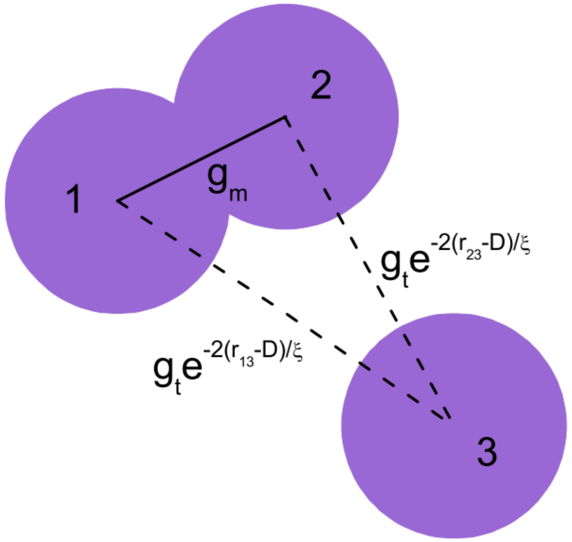
$$\sigma(T) \propto \exp\left(-\sqrt{\frac{T_0}{T}}\right)$$

Weak transition between dielectric and metallic regimes; $\Delta\sigma \approx 10$ at the percolation threshold

S.J. Gilbert *et al.*, J. Phys. Condens. Matter **34**, 204007 (2022).

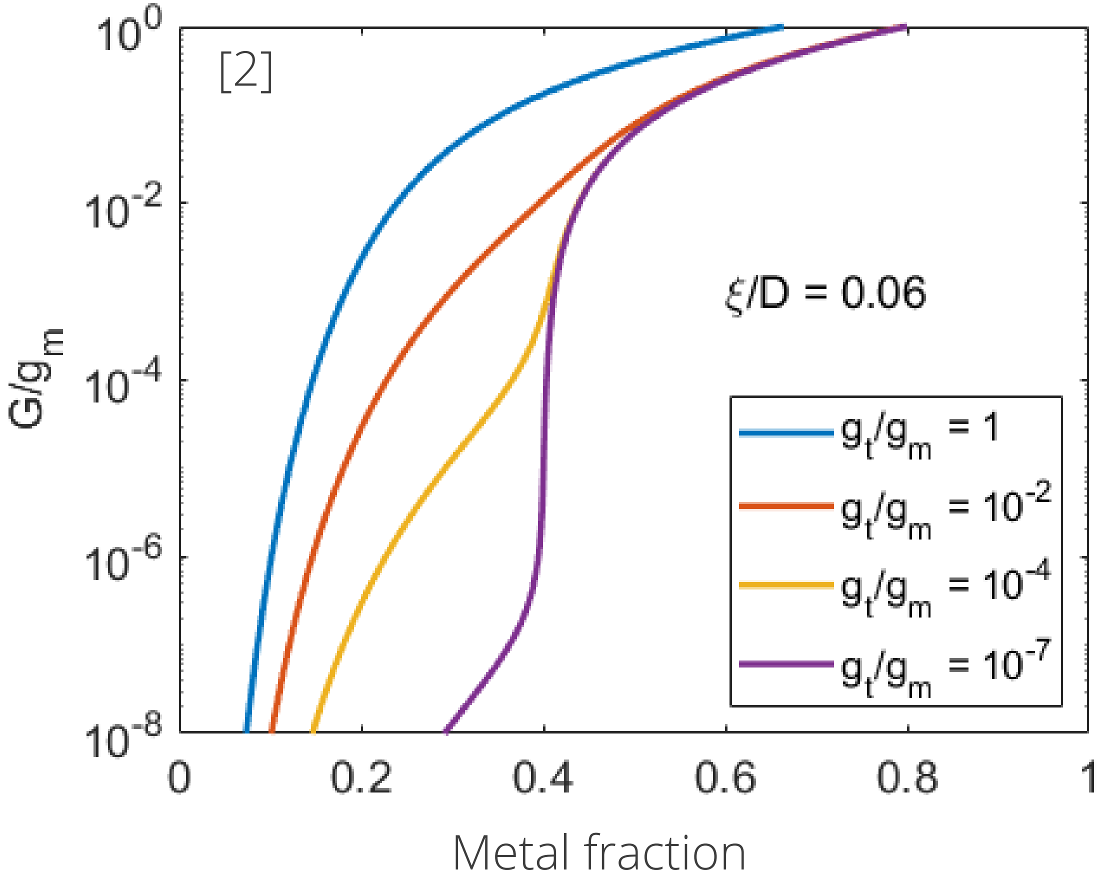
Conductivity change at the percolation threshold dependent on interface interactions

Grimaldi[1] proposed that conductivity depends on the ratio of tunneling (g_t) and metal (g_m) conductivities.



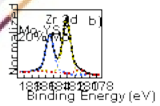
Island diagram
D, ~ 1—10 nm
Tunneling decay length
ξ, ~ 0.1 – 1 nm

$$\frac{\left(\frac{\varphi}{\varphi_c}\right) g_m^{1/t}}{G^{1/t} + g_m^{1/t}} + 4\varphi\left\{\left[1 + \frac{\xi}{2D}\ln\left(\frac{g_t + G}{G}\right)\right]^3 - 1\right\} = 1$$



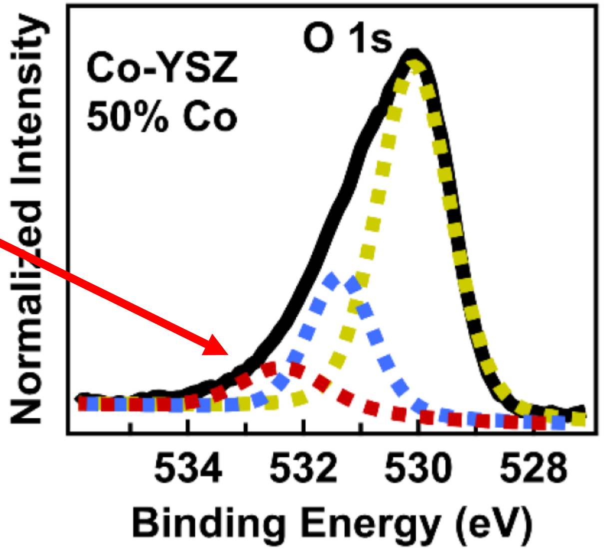
[1] Grimaldi, Phys. Rev. B **89**, 214201 (2014). [2] S.J. Gilbert *et al.*, J. Phys. Condens. Matter **34**, 204007 (2022).

Interface interactions explain conductivity trends



Zr^{2+} from oxygen vacancies

Metal-oxide interface states



Reference	Metal	Insulator	$\Delta\sigma_{\varphi c \pm 0.05}$
This work	Mo	YSZ	10^1
This work	Co	YSZ	10^1
Stogneĭ[1]	Co	Al_2O_n	10^2
Niklasson[2]	Co	Al_2O_3	10^7
Barzilai[3]	Co	SiO_2	10^2
Zhu[4]	Fe	Al_2O_3	10^2
Aronzon[5]	Fe	SiO_2	10^2
Honda[6]	Fe	SiO_2	10^3
Gittleman[7]	Ni	SiO_2	10^2
Toker[8]	Ni	SiO_2	10^2
Abeles[9]	Ni	SiO_2	10^2
Milner[10]	Ni	SiO_2	10^4
Abeles[11]	W	Al_2O_3	10^2
Wei[12]	Ag	SnO_2	10^1
Balberg[13]	Ag	Al_2O_3	10^2
Cohen[14]	Ag	SiO_2	10^4
Priestley[15]	Ag	SiO_2	10^5
Abeles[9]	Au	Al_2O_3	10^6
Cohen[14]	Au	SiO_2	10^4
McAlister[16]	Au	SiO_2	10^8

Conductivity change across percolation threshold.

Non-noble metals typically 10^2-10^3

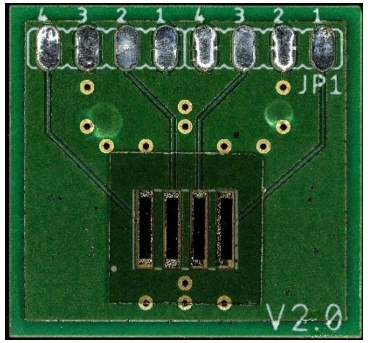
Noble metals typically $\geq 10^4$

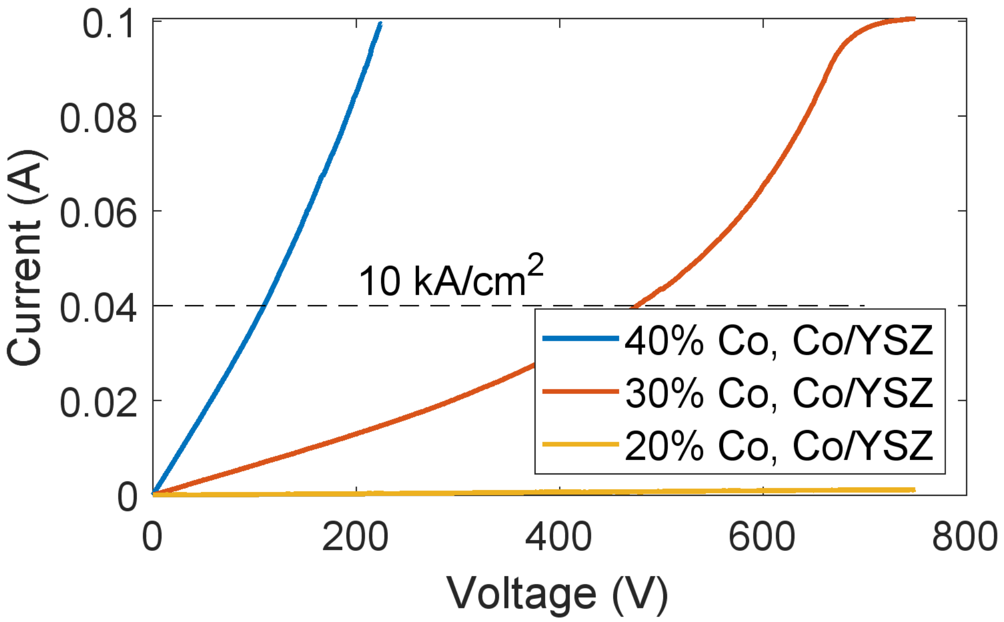
Please see S.J. Gilbert *et al.*, J. Phys. Condens. Matter **34**, 204007 (2022) for reference citations.

Granular metals are suitable for high E-field applications

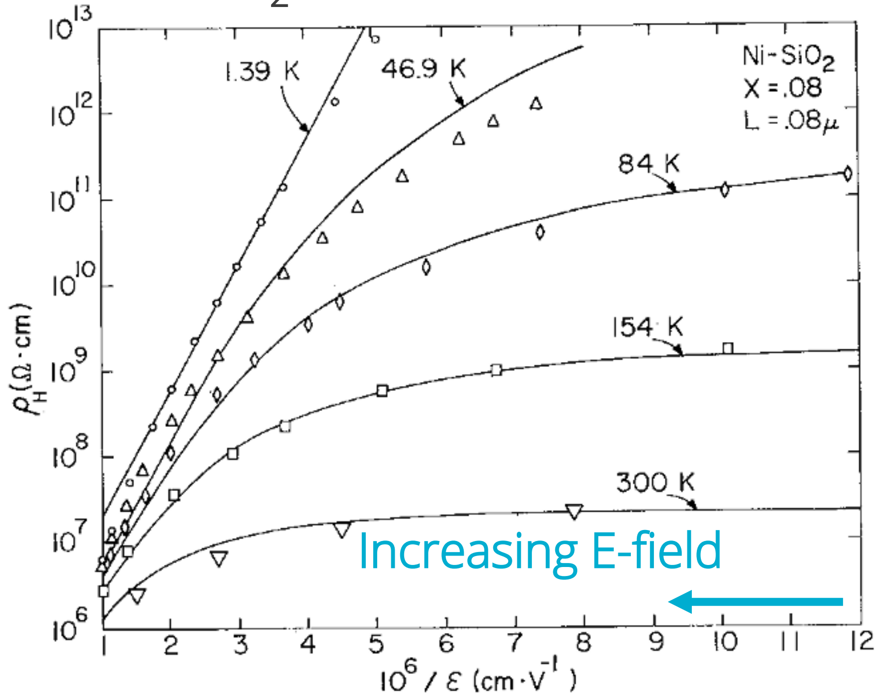
> 5 kV/cm demonstrated in lateral devices

> 0.1 MV/cm in vertical devices





Ni/SiO_2



10^6 V/cm

10^5 V/cm

Field-enhanced tunneling

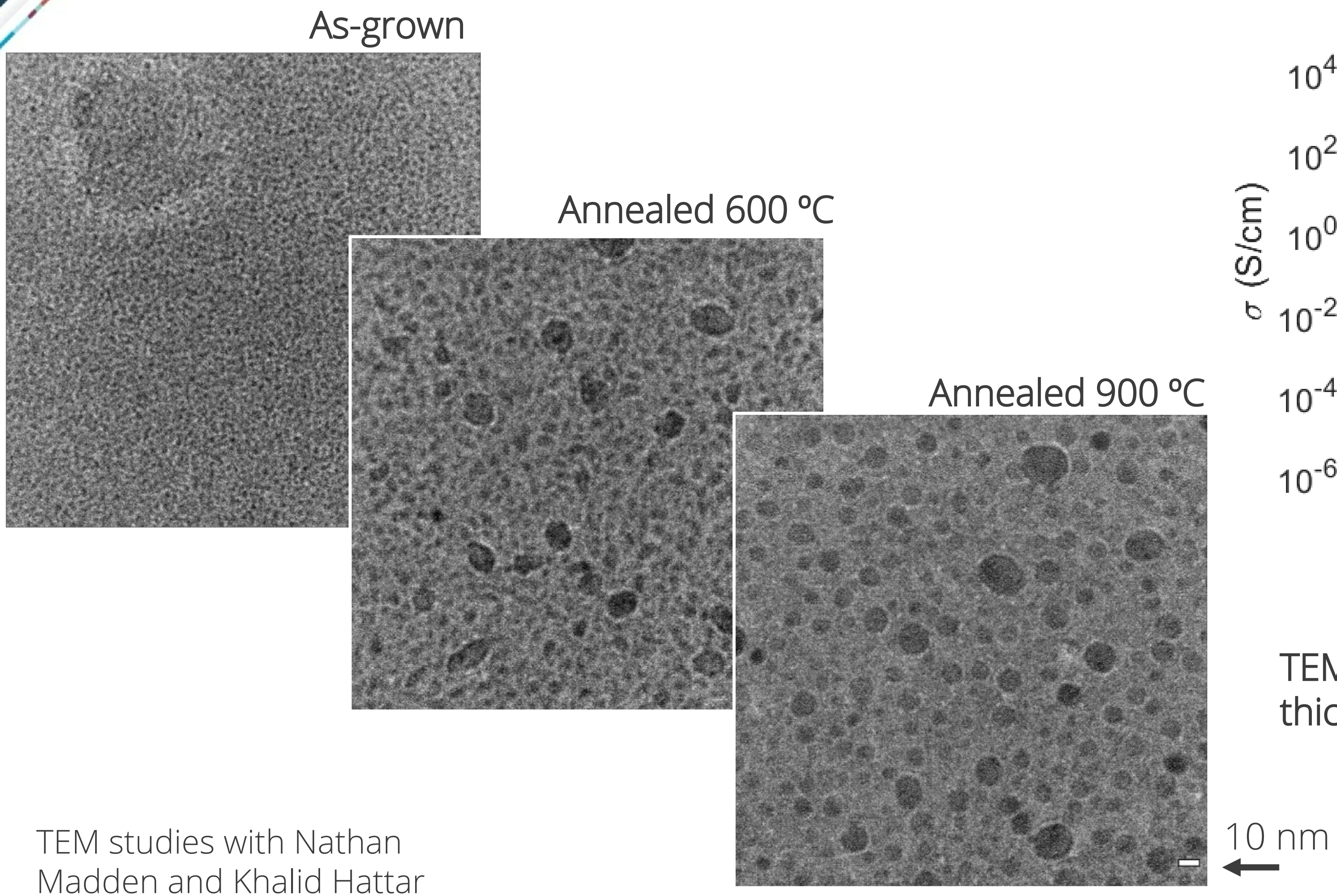
$\sigma_{H,DC} \propto \exp(\mathcal{E}_0/E)$ for $e\Delta V > k_B T$

Fowler-Nordheim tunneling

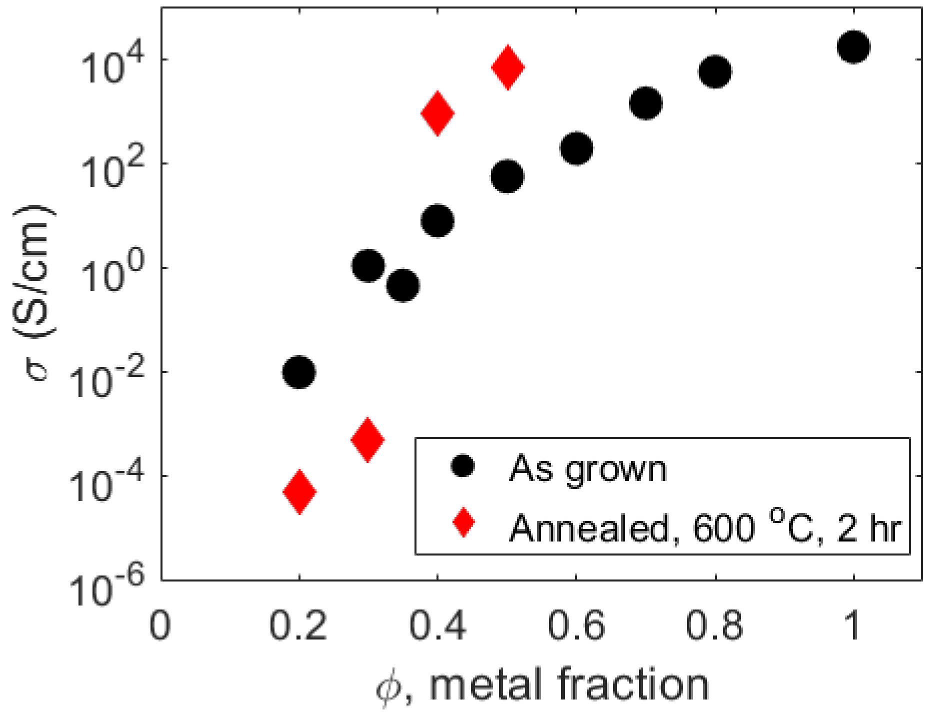
$\sigma_{FN,DC} \propto \exp(1/E)$ for $e\Delta V >$ tunneling barrier height

[1] Abeles *et al*. Adv. in Phys. **24**, 407 (1975)

Annealing drives island coalescence and should mitigate interface effects



Co-YSZ

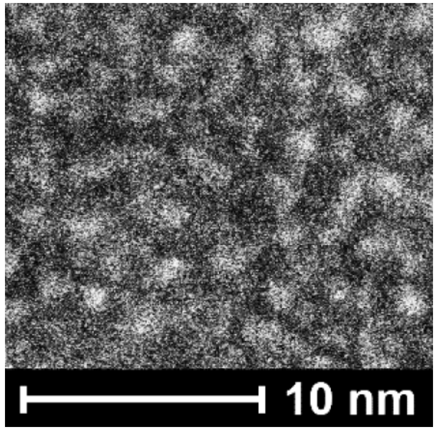


TEM images of 5 nm thick Co-YSZ

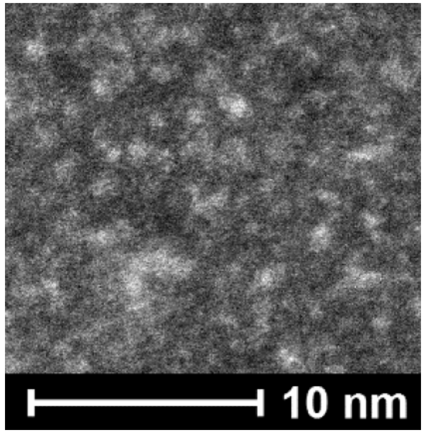
TEM studies with Nathan Madden and Khalid Hattar

Conclusion: Controlling interface interactions is crucial for controlling granular metal conductivity

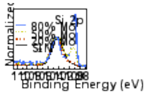
Mo-YSZ, φ = 0.2



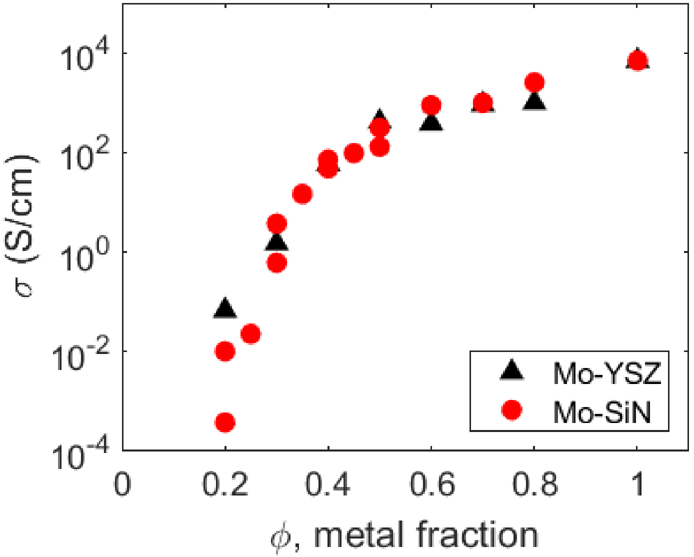
Mo-SiN, φ = 0.2



Mo-SiN$_x$



Mo-silicide formation



Acknowledgements

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80 dB drop in impedance achieved in Mo-SiN granular metal