SAND2024-08910C

Sandia National Laboratories

Exceptional service in the national interest

Nanostructured Materials to Negate Nanosecond Voltage Spikes

Simeon Gilbert

April 24th, 2024

Emergent Quantum Materials and Technologies (EQUATE) Seminar

University of Nebraska – Lincoln

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

U.S. DEPARTMENT OF ENERGY

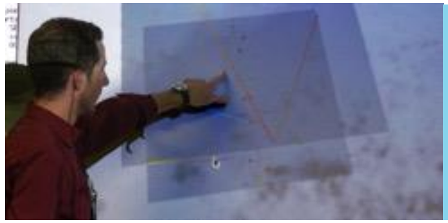
NNSA

Focus Areas at Sandia National Laboratories

Global Security

Nuclear Deterrence

National Security Programs



Advanced Science & Technology

Energy & Homeland Security

RESILIENT ENERGY SYSTEMS MISSION CAMPAIGN

Granular Metal Team

PI: Laura Biedermann

Granular metal growth: Simeon Gilbert, Michael Siegal, Doug Vodnik, Lyle Brunke

Granular metal electrical characterization: Michael McGarry, Will Bachman, Peter Sharma, Tyler Bowman, Luke Yates

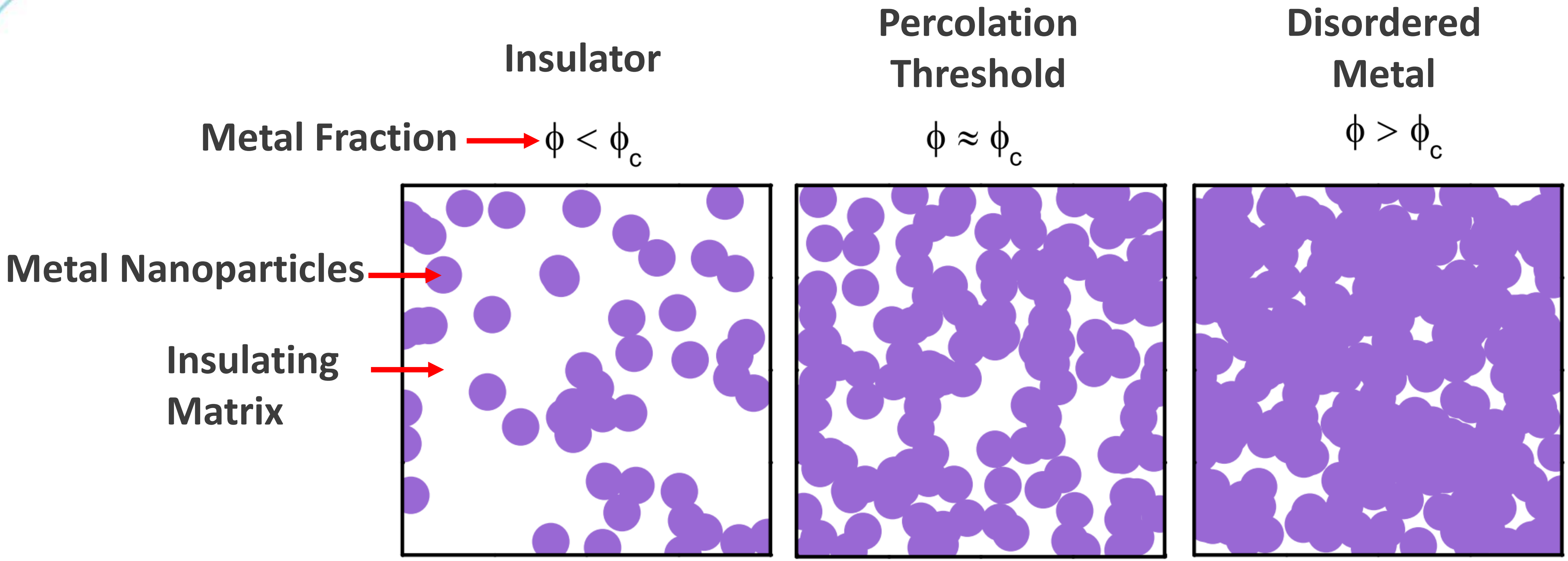
Microscopy and spectroscopy: Simeon Gilbert, Melissa Meyerson, Paul Kotula, Samantha Rosenberg, Tommy Kmieciak

Device and PCB design: Jack Flicker, Rachid Darbali-Zamora, Will Bachman

Lithography and packaging: Patrick Finnegan, Scott Weathered, Adrian Cassias, Connor Healey, Alvin Ha

This work was supported by the Laboratory Directed Research and Development program at Sandia National Laboratories. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

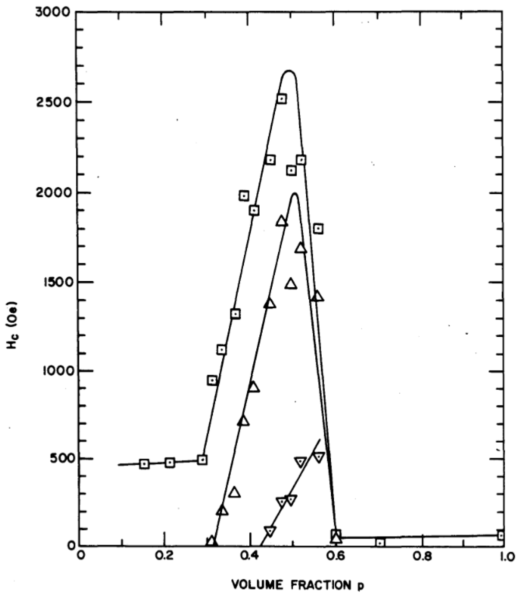
What are granular metals (GMs)?



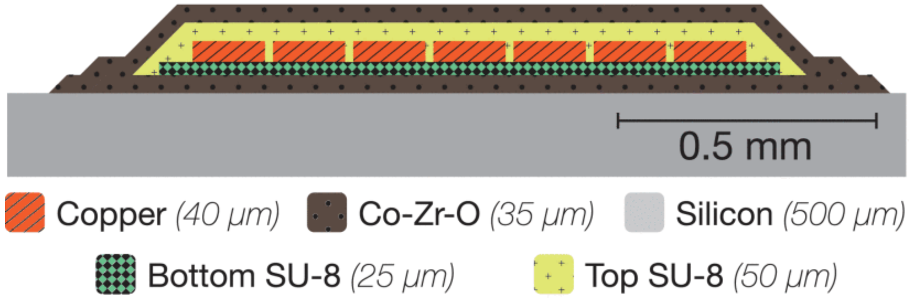
Grimaldi, Phys. Rev. B **89**, 214201 (2014)

Applications of Granular Metals

Magnetic Materials

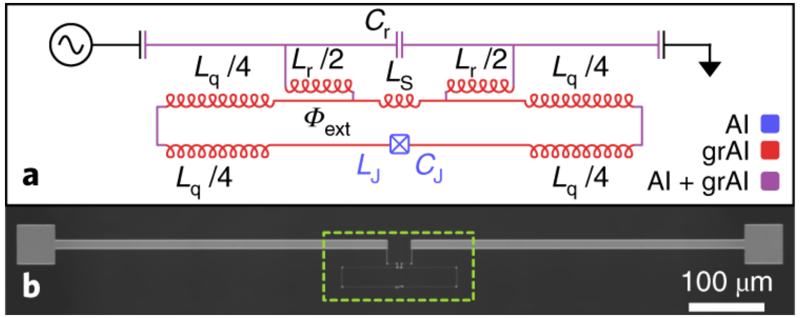


S. H. Liou and C. L. Chien; Granular metal films as recording media. *Appl. Phys. Lett.* **52**, 512 (1988)



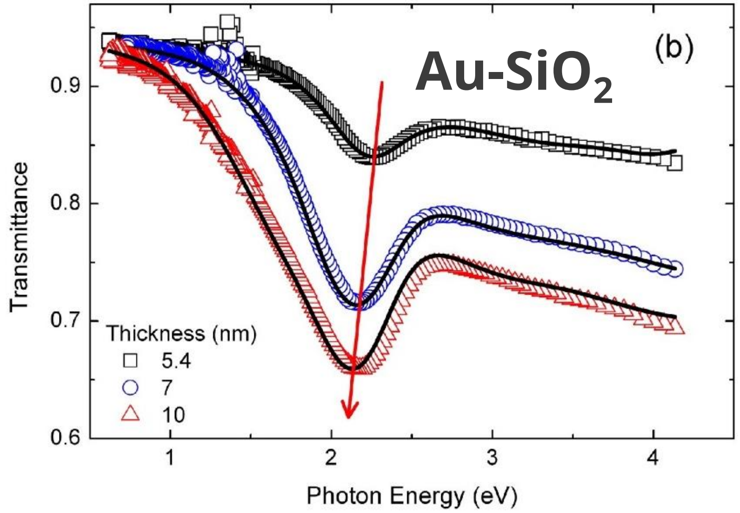
D. V. Harburg *et al.*, *IEEE Journal of Emerging and Selected Topics in Power Electronics* 6, 1280 (2018)

Superconducting Circuits



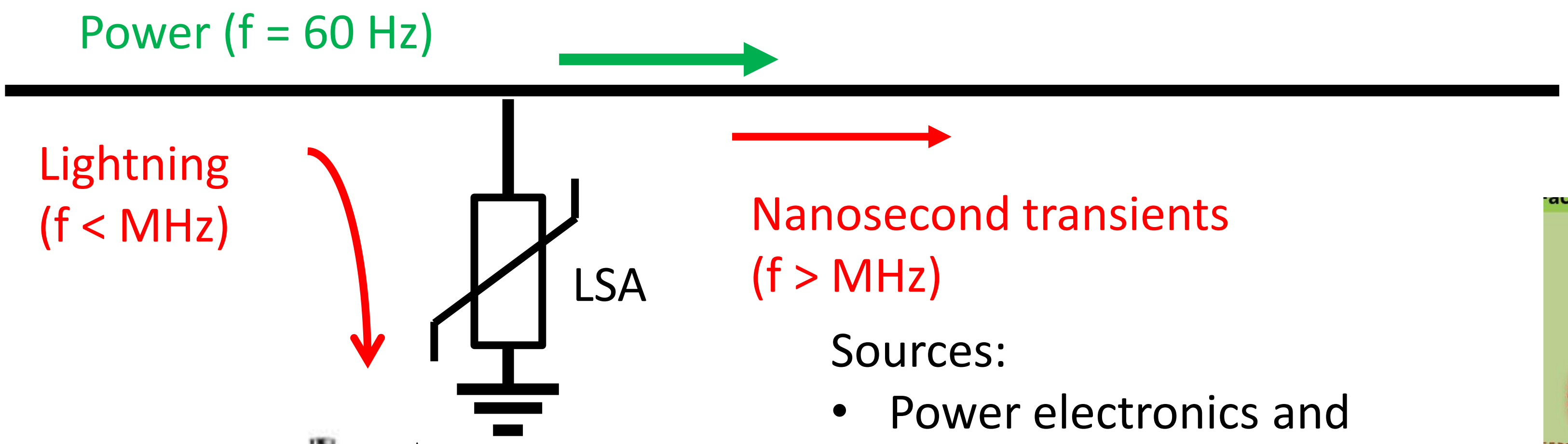
L. Grünhaupt *et al.*, *Nat. Mater.* 18, 816 (2019)

Plasmonics



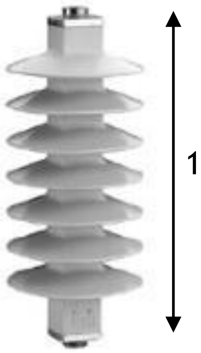
H. Bakkali, et al. Applied Surface Science 405, 240 (2017)

Nanosecond high-voltage transients threaten electrical grid reliability



Sources:

- Power electronics and gas-insulated substation switching events
- Insulation faults
- Nuclear EMPs



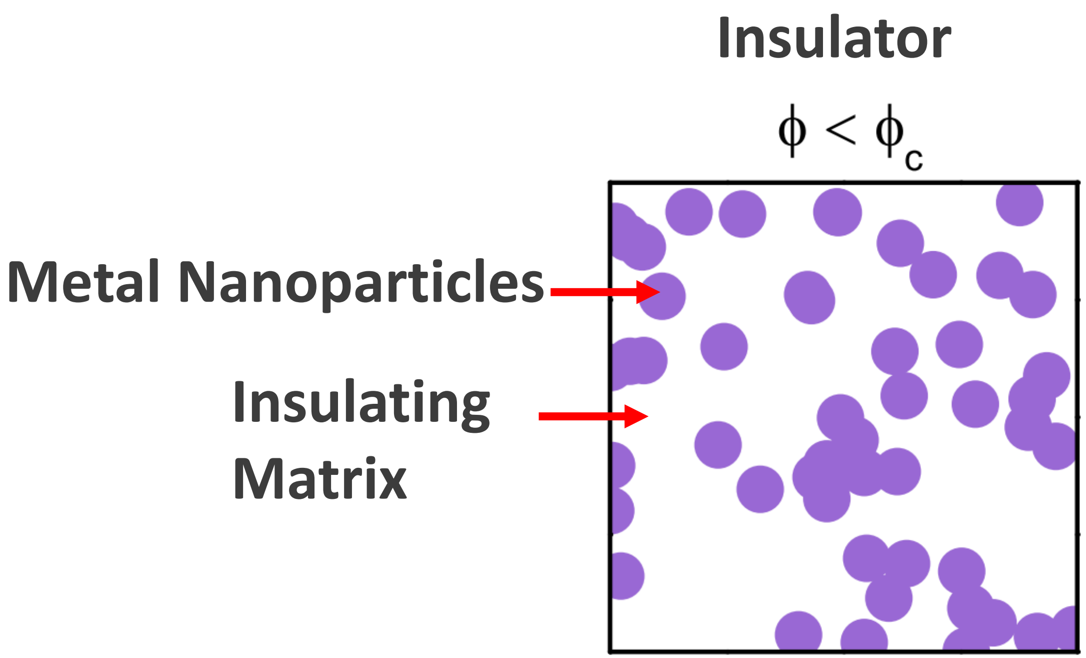
Lightning surge arresters'(LSAs) response time is ~100 ns

vulnerable infrastructure

An additional ns arrester is needed with

- High breakdown strength for compact devices
- Low conductivity, σ, at grid voltages and frequencies
- High σ at MHz/GHz frequencies and with overvoltages
- High thermal stability
- Large current carrying capacity (>1 kA/cm^2)

Granular metals are promising for ultrafast grid protection.



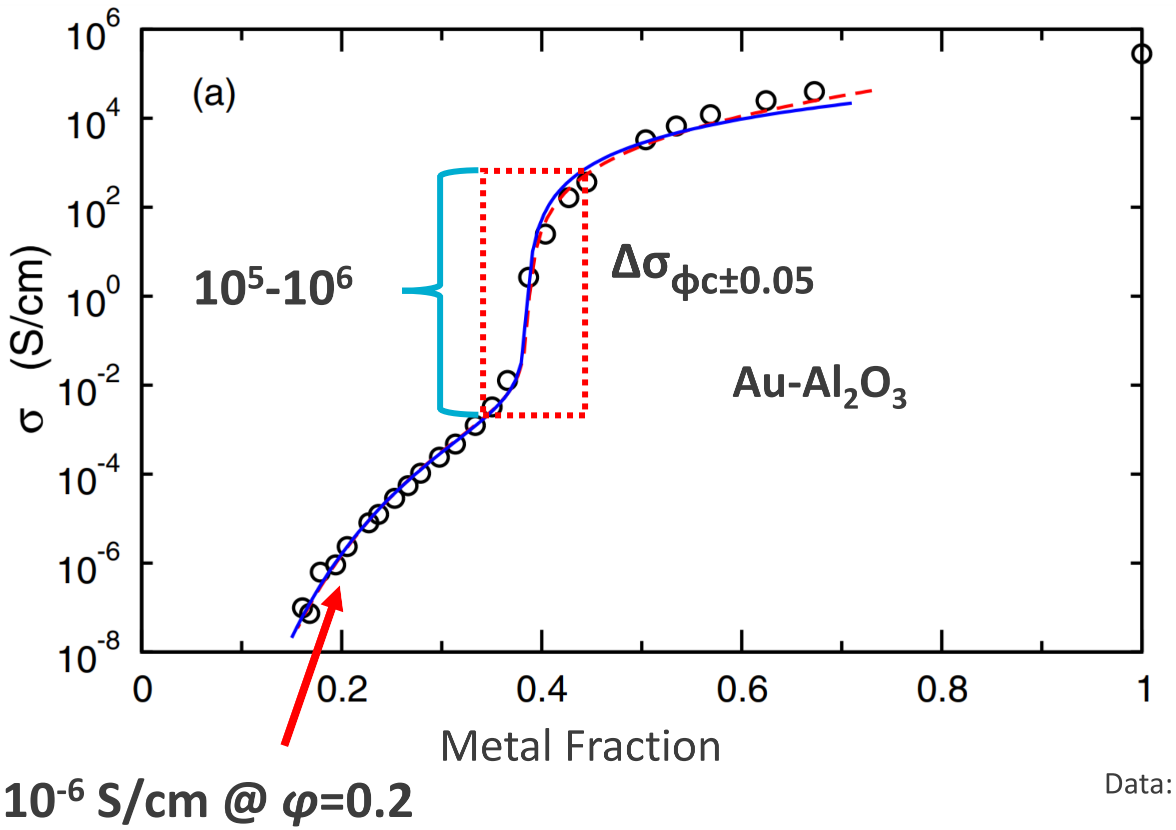
Grimaldi, Phys. Rev. B **89**, 214201 (2014)

Below φ_c conduction occurs via electron tunneling and capacitive transport.

Conduction from electron tunneling increases at higher electric fields.

Conduction from capacitive transport increases at higher frequencies.

GMs have desired low DC conductivity.

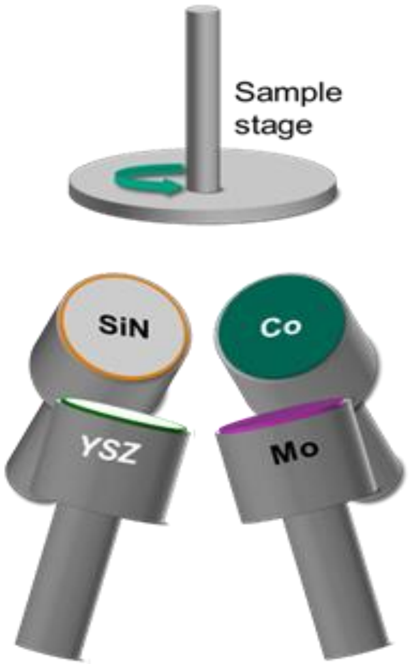


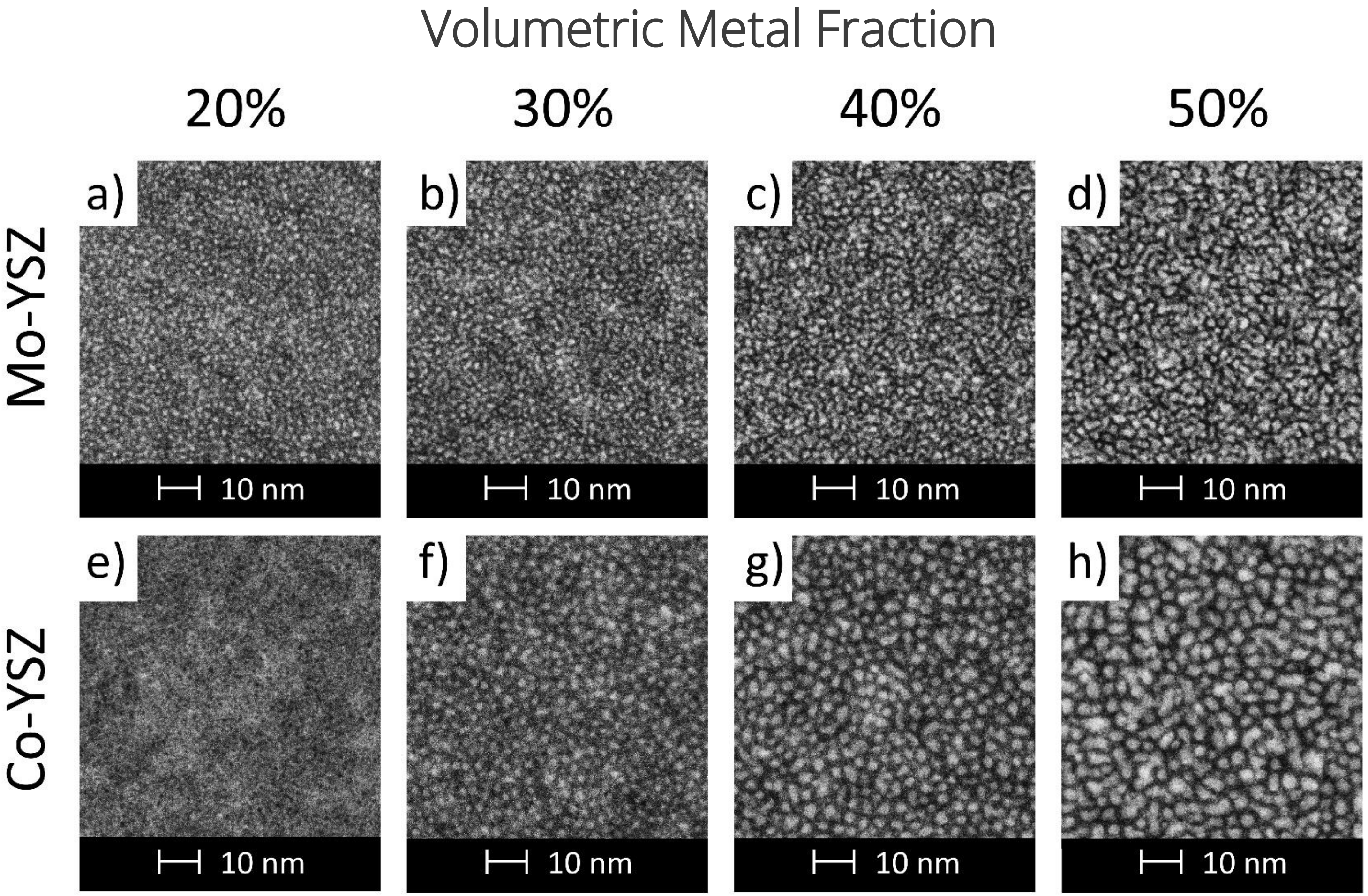
Data: Abeles et al. Adv. in Phys. **24**, 407 (1975)

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

Conductivities of <10^{-5} S/cm are desired to reduce leakage currents.

Co-YSZ and Mo-YSZ synthesized by RF co-sputtering in Ar



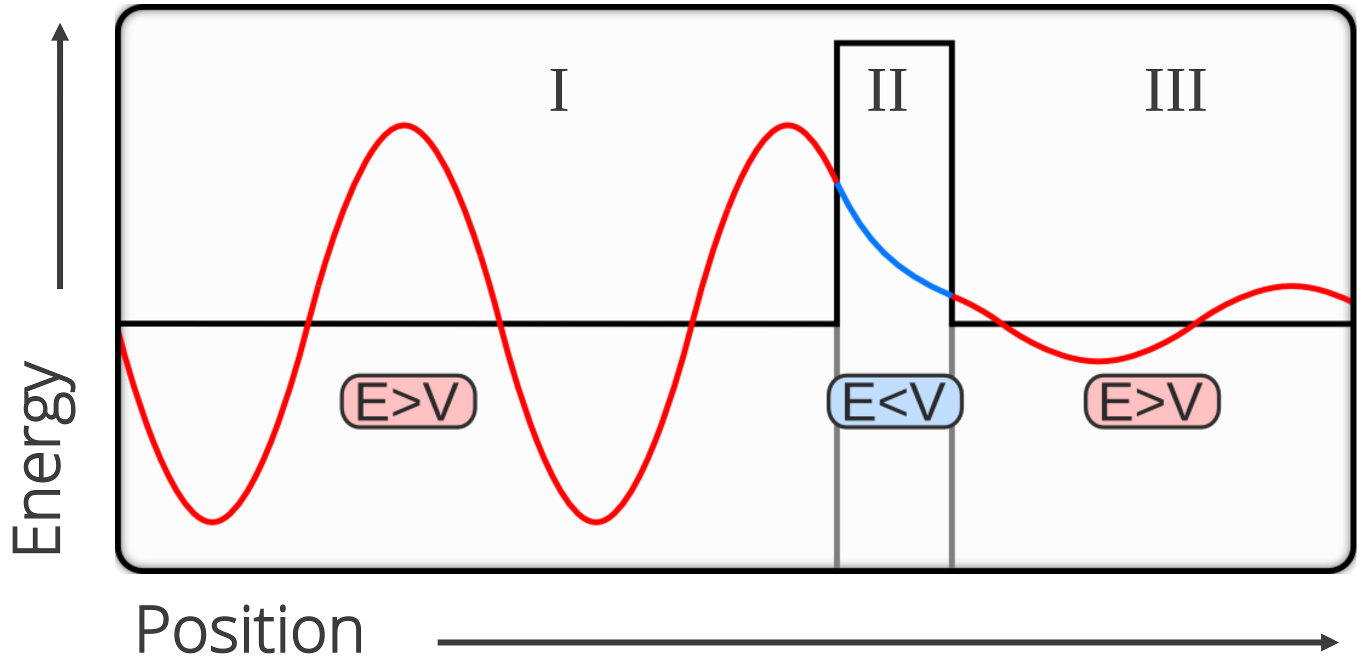


Metal island diameters between 1-3 nm.

Particle separation distances are ~0.2 - 0.6 nm

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

Quantum Tunneling



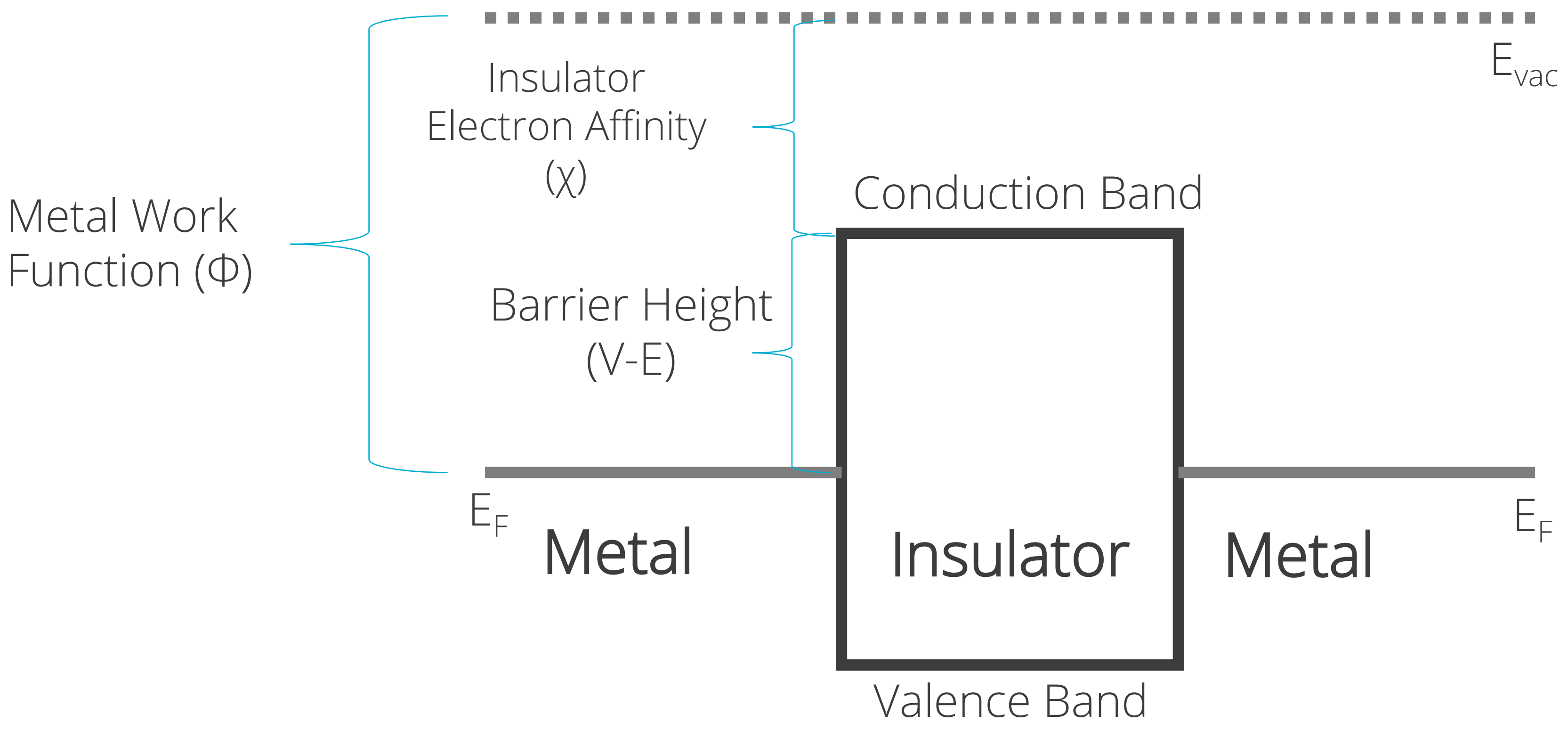
$$\Psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & , \text{ I} \\ Ce^{\kappa x} + De^{\kappa x} & , \text{ II} \\ Fe^{ikx} & , \text{ III} \end{cases}$$

Tunneling Probability Decay Length

$$\kappa = \sqrt{\frac{2m(V-E)}{\hbar^2}}$$

Image from https://upload.wikimedia.org/wikipedia/commons/1/1d/TunnelEffektKling1.png under Creative Commons licensing for reuse and modification.

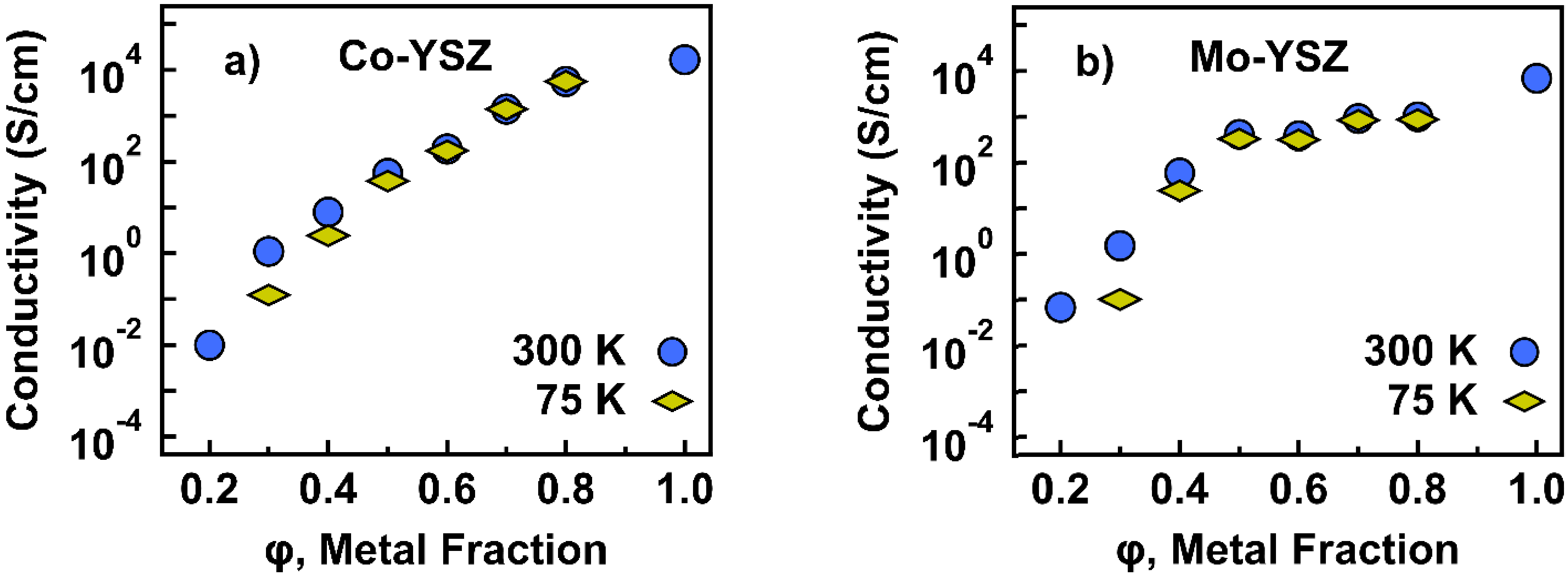
Quantum tunneling in granular metals



Tunneling Probability Decay Length

$$\kappa = \sqrt{\frac{2m(V-E)}{\hbar^2}} = \sqrt{\frac{2m(\Phi-\chi)}{\hbar^2}} = 0.1 - 0.2\ nm$$

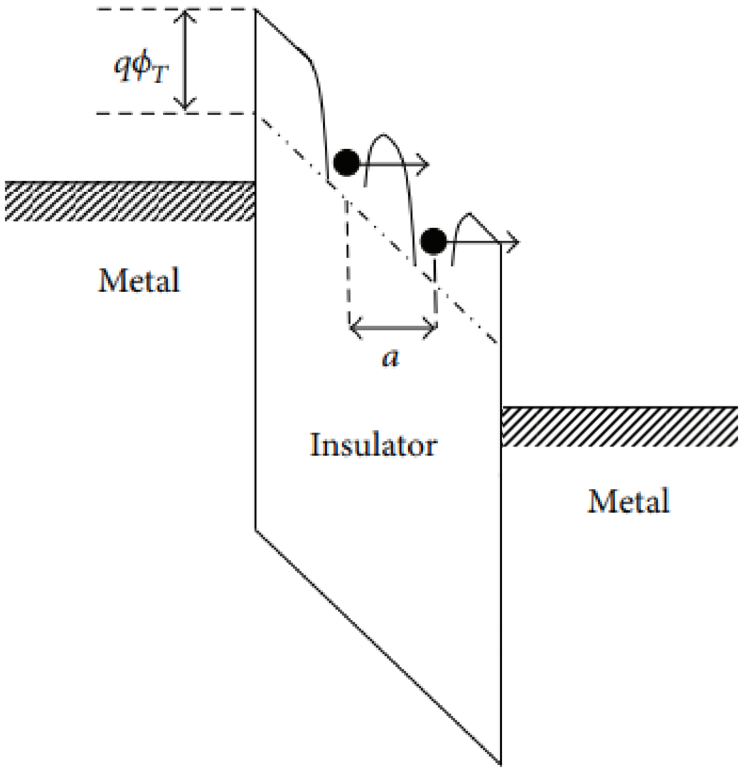
Co-YSZ and Mo-YSZ have high DC conductivities.



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

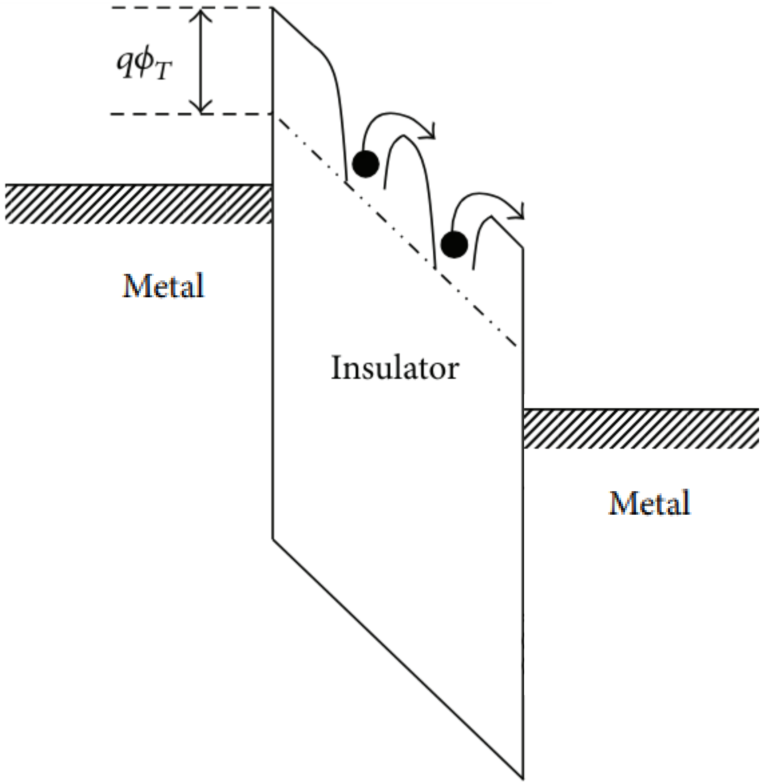
Potential tunneling mechanisms

Hopping Conduction



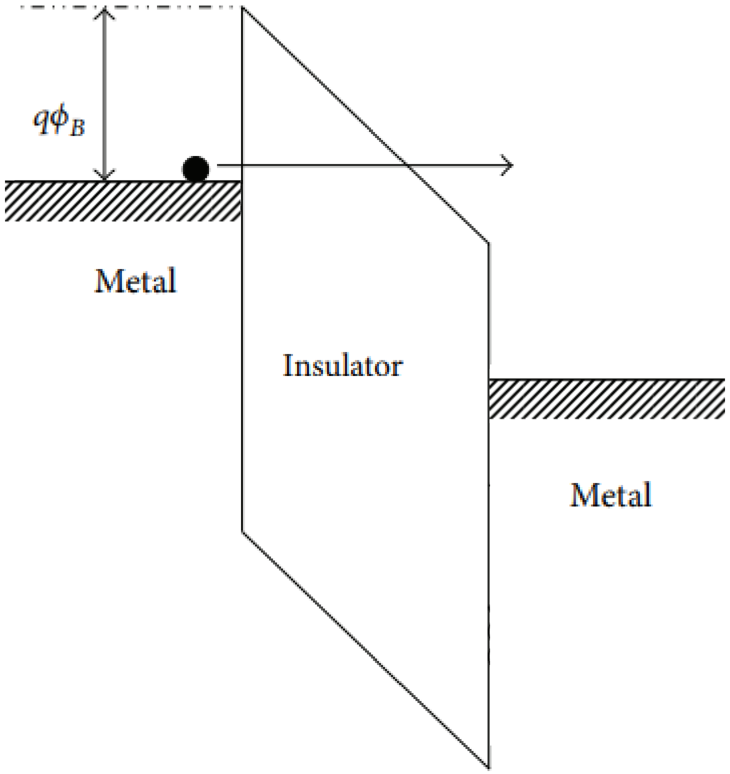
$$\sigma \propto \exp\left(-2\sqrt{E_A/k_B T}\right)$$

Poole-Frenkel Emission



$$\sigma \propto \exp\left[(q/k_B T)\sqrt{qE/\mathcal{E}_0\mathcal{E}_r}\right]$$

Fowler-Nordheim Tunneling

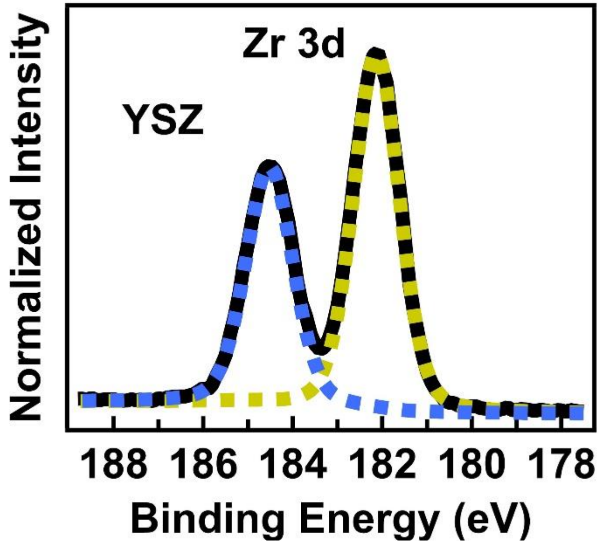


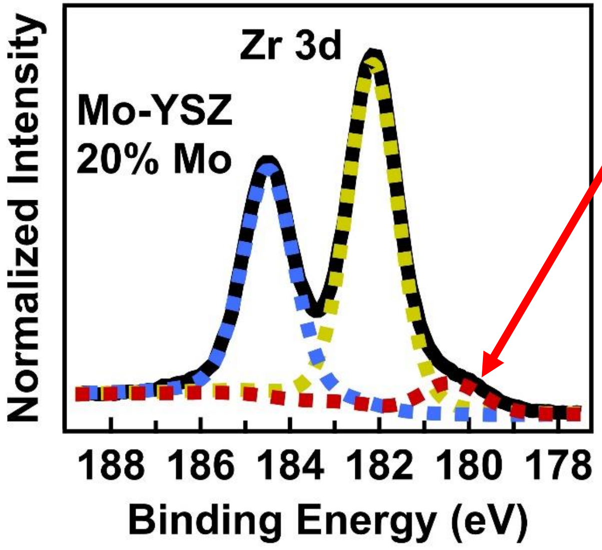
$$\sigma \propto \mathrm{E}^2 \exp(E_0/E)$$

Conductivity depends on defect density, temperature and electric field.

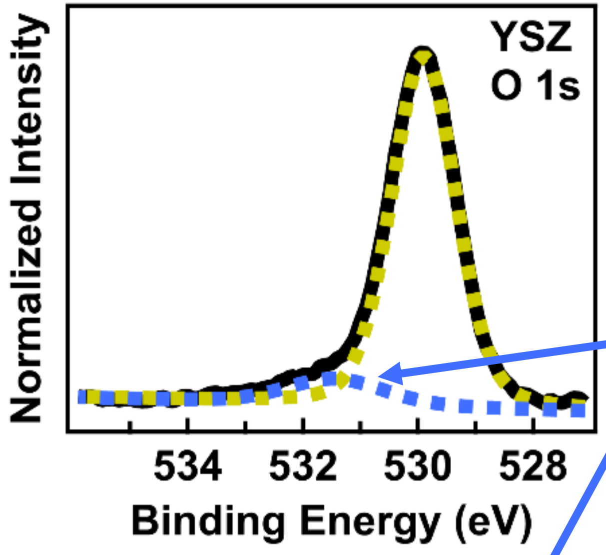
Fu-Chien Chiu, Advances in Materials Science and Engineering, **2014**, 578168, (2014)

X-ray photoemission spectroscopy shows metal-oxide formation



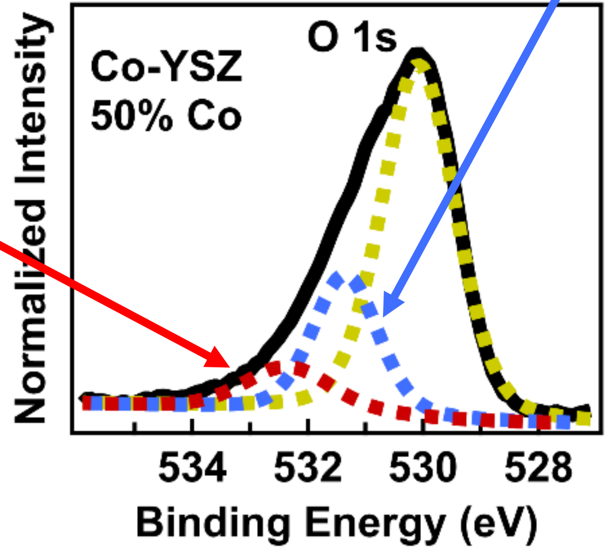


Zr^{2+} from oxygen vacancies



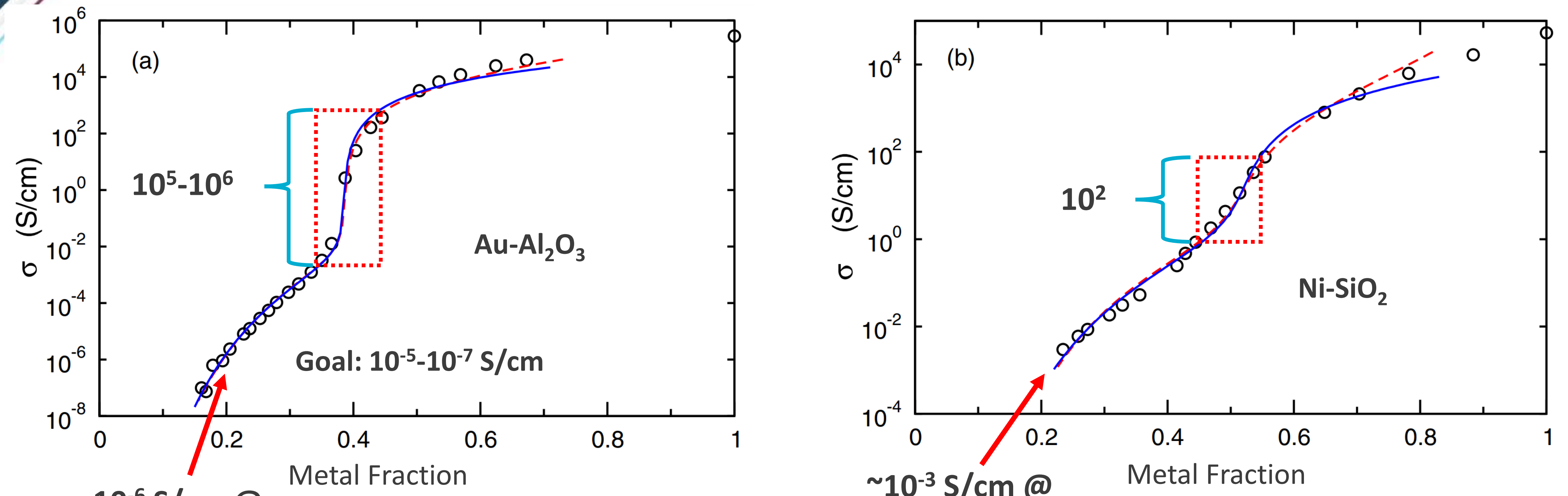
Surface oxygen in YSZ

Metal-oxide interface states



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

Noble Metal GMs have desired low DC conductivity.



10^{-6} S/cm @ φ=0.2

~10^{-3} S/cm @ φ=0.2

Data: Abeles et al. Adv. in Phys. **24**, 407 (1975)

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

Noble metals are expensive and have lower than desired thermal stabilities.

Nearly all granular metals utilize oxide insulators.

Metal-oxide formation reduces GM performance.

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
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.

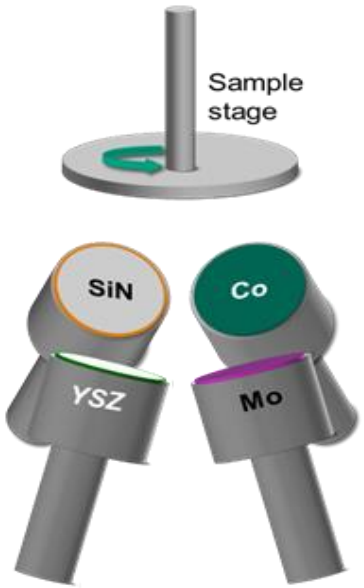
Non-noble metals typically 10^2-10^3

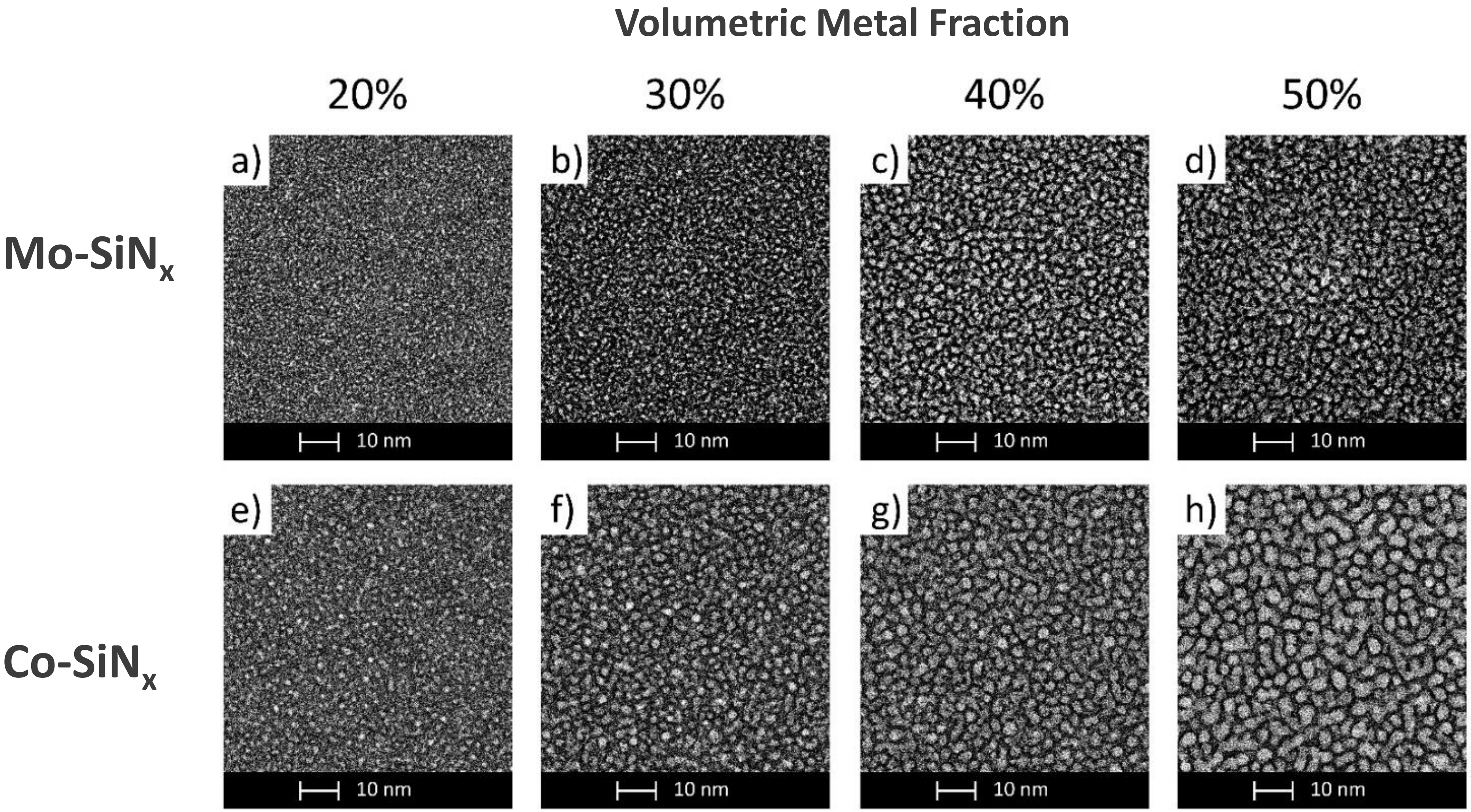
Noble metals typically ≥10^4

[1]Stogneĭ et al. Phys. Solid State **49**, 164 (2007)
[2]Niklasson et al. J. Appl. Phys. **55**, 3382 (1984)
[3]Barzilai et al. Phys. Rev. B **23**, 1809 (1981)
[4]Zhu et al. Phys. Rev. B **60**, 11918 (1999)
[5]Aronzon et al. Phys. Solid State **41**, 857 (1999)
[6]Honda et al. Phys. Rev. B **56**, 14566 (1997)
[7]Gittleman et al., Phys. Rev. B **5**, 3609 (1972)
[8]Toker et al. Phys. Rev. B **68**, 041403(R) (2003)
[9]Abeles et al. Adv. in Phys. **24**, 407 (1975)
[10]Milner et al. Phys. Rev. Lett. **76**, 475 (1996)
[11]Abeles et al. Phys. Rev. Lett. **35**, 247 (1975)
[12]Wei et al. Appl. Phys. Lett. **102**, 131911 (2013)
[13]Balberg et al. Eur. Phys. J. B **86**, 428 (2013)
[14]Cohen et al., Phys. Rev. B **8**, 3689 (1973)
[15]Priestley et al. Phys. Rev. B **12**, 2121 (1975)
[16]McAlister et al. J. Phys. C: Solid State Phys. **17**, L751 (1984)

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

Co-SiN_x and Mo-SiN_x GMs were synthesized by RF co-sputtering.

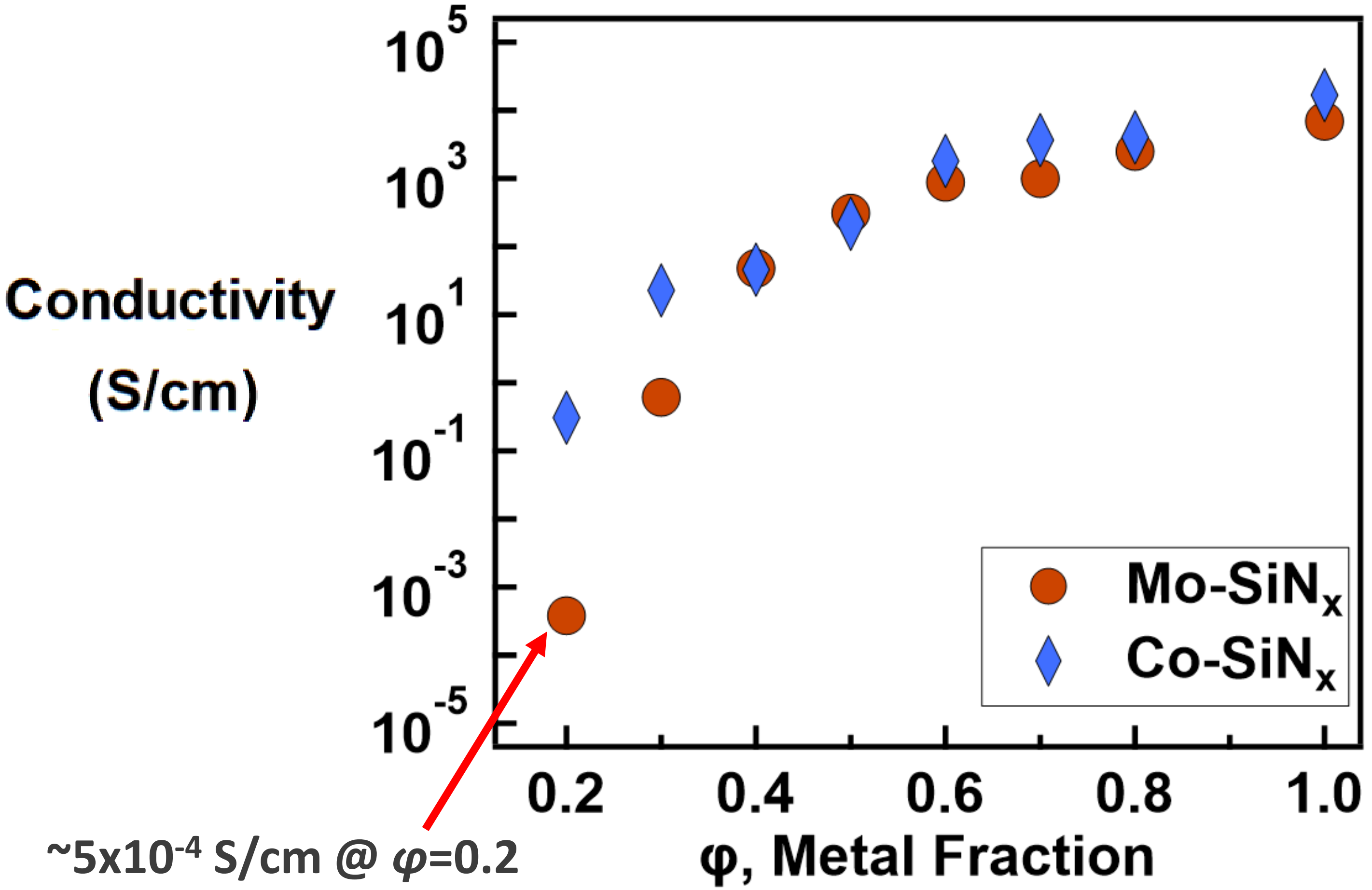




S.J. Gilbert et al., Nanotechnology, **34**, 415706 (2023)

Nanoparticle diameters and separations are similar to YSZ GMs.

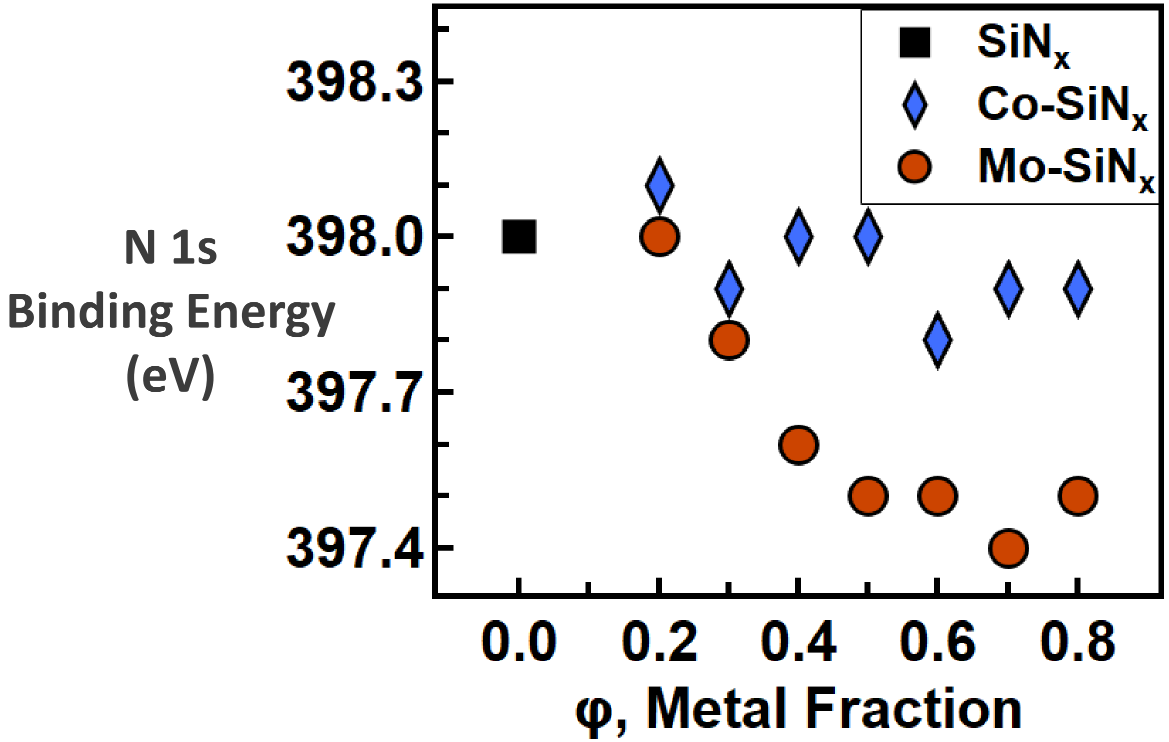
Conductivity still too high for electrical grid integration.



Target conductivity is 10^{-5} - 10^{-8} S/cm

S.J. Gilbert et al., Nanotechnology, **34**, 415706 (2023)

Mo-SiN_x exhibits Mo-nitride formation.

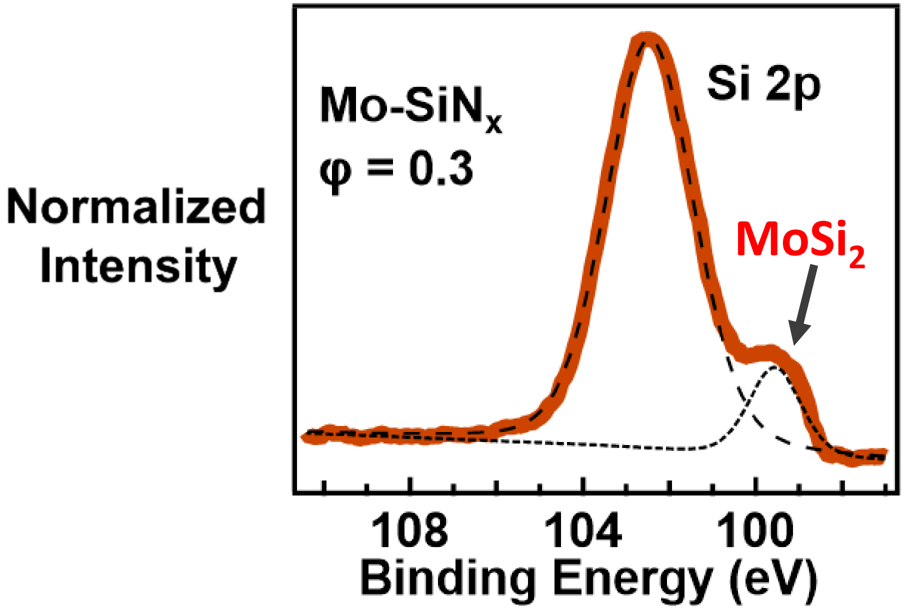


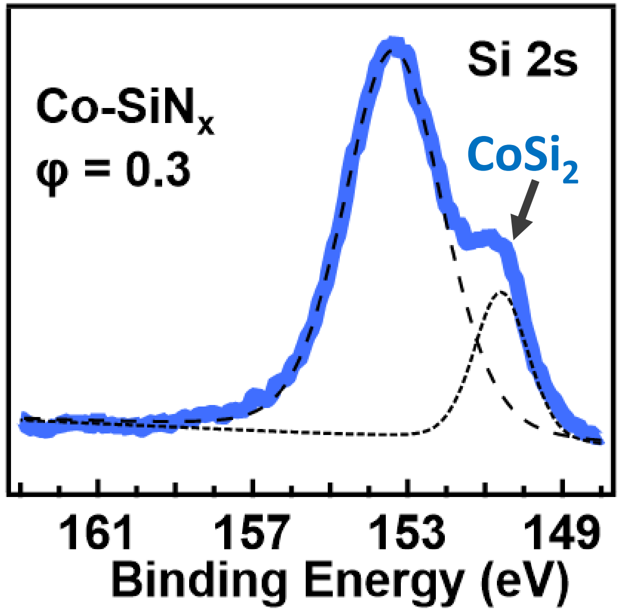
S.J. Gilbert et al., Nanotechnology, **34**, 415706 (2023)

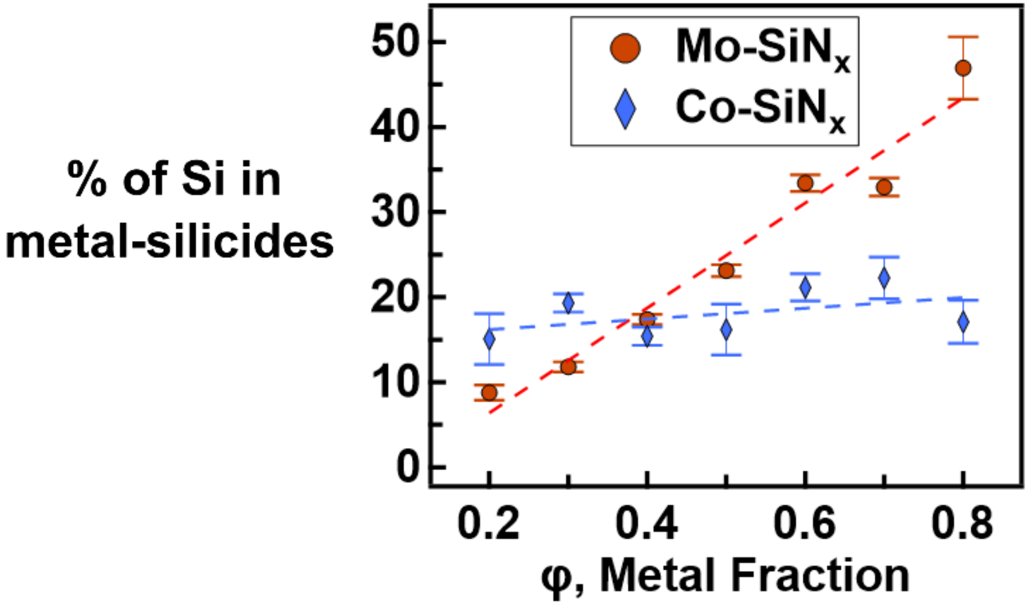
Group	Compound	ΔH (kJ*mol^{-1}*atom^{-1})	Reference
Mo-Nitrides	Mo_2N	-41	1
	MoN	-51	1
Co-Nitrides	Co_4N	+3	2
	Co_2N	-9	1
	CoN	0	1

1. A. K. Niessen et al., Journal of the Less Common Metals **82**, 75-80 (1981).
2. I. K. Milad et al., Catalysis Letters **52**, 113-119 (1998).

Nitrogen vacancies cause metal-silicide formation and increase conductivity.







S.J. Gilbert et al., Nanotechnology, **34**, 415706 (2023)

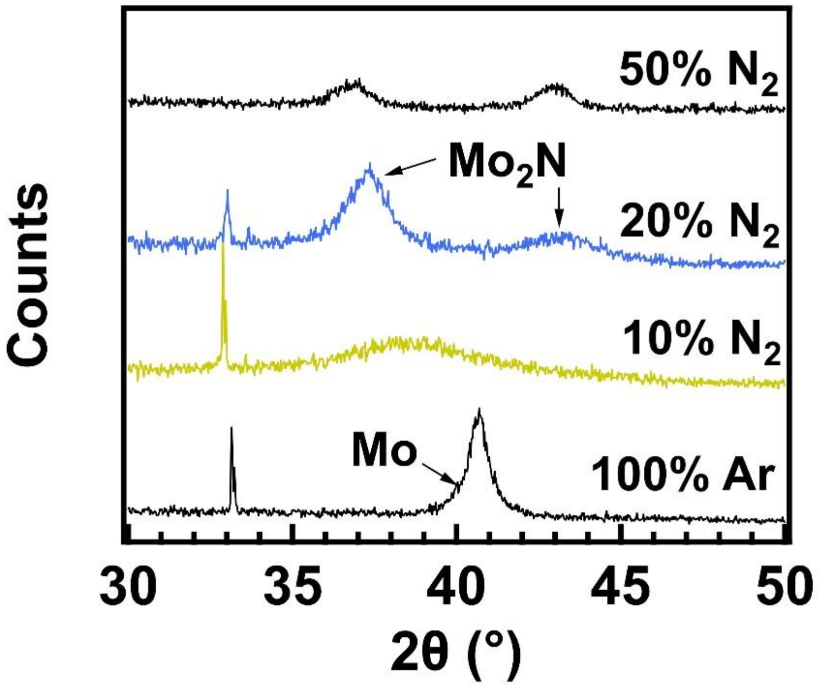
Target	Sputtering gas	$\rho_{(300K)}$ (Ω cm)
β-Si_3N_4	100%Ar	1.7×10^{10}
	80%Ar–20N_2	1.1×10^{11}
	50%Ar–50N_2	3.4×10^{14}
	20%Ar–80N_2	1.3×10^{13}
	100N_2	6.2×10^{12}

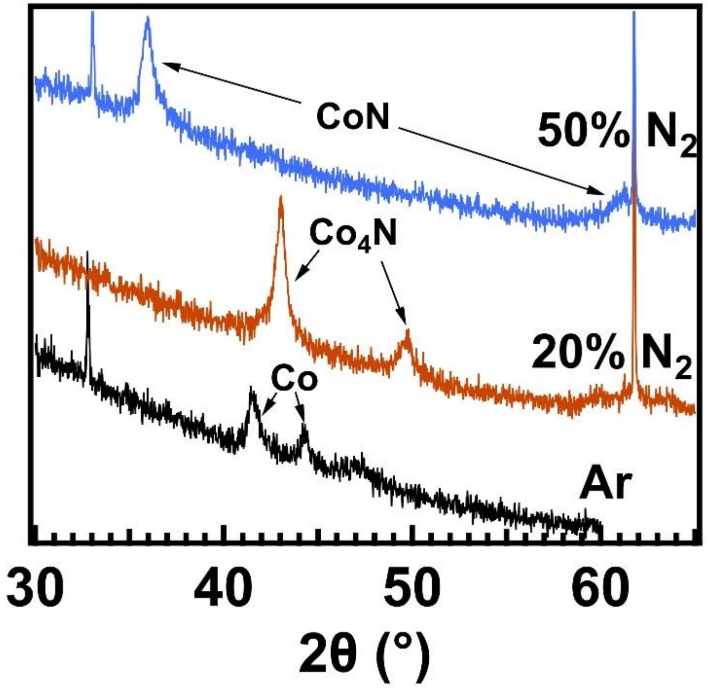
Vila et al. Thin Solid Films **459**, 195 (2004)

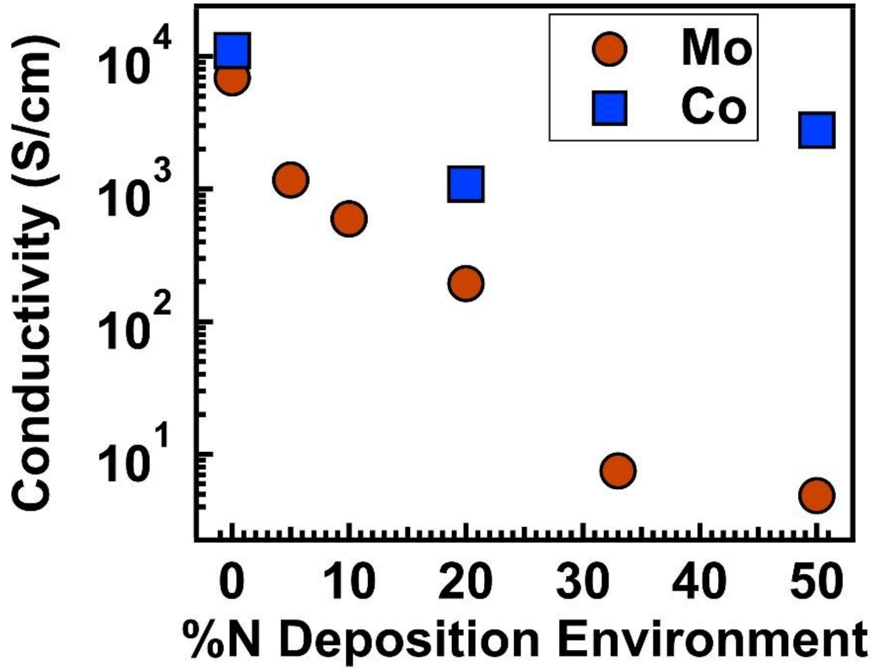
Insulator can be repaired by depositing in Ar/N_2.

Sputtering metals in N_2 results in metal-nitrides.

X-ray diffraction







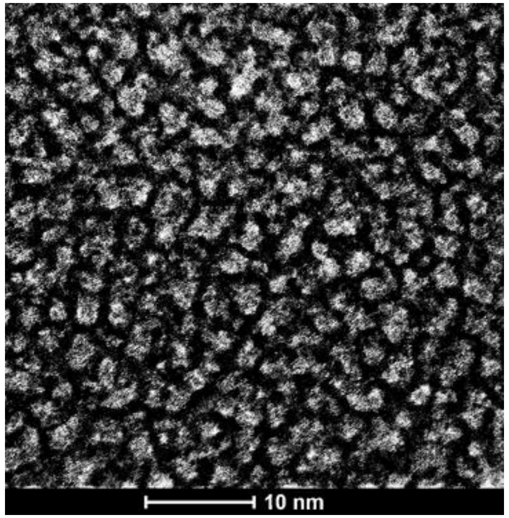
Selected environments
Mo-SiN_x: 10% N_2
Co-SiN_x: 50% N_2

M. McGarry et al., submitted

Deposition in N_2 Reduces Nanoparticle Size

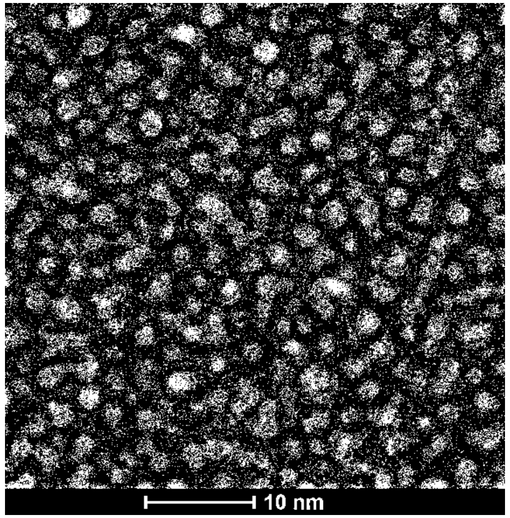
Mo-SiN_x (ϕ=0.5)

100% Ar



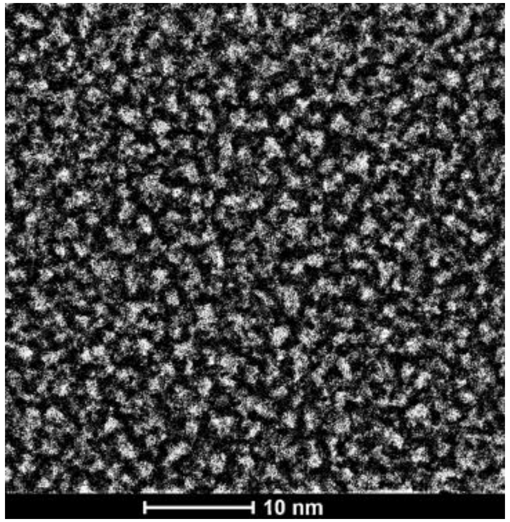
Co-SiN_x (ϕ=0.3)

100% Ar



Mo-SiN_x (ϕ=0.5)

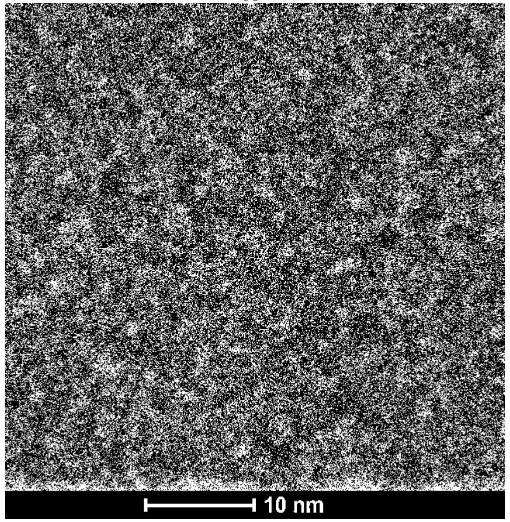
10% N_2



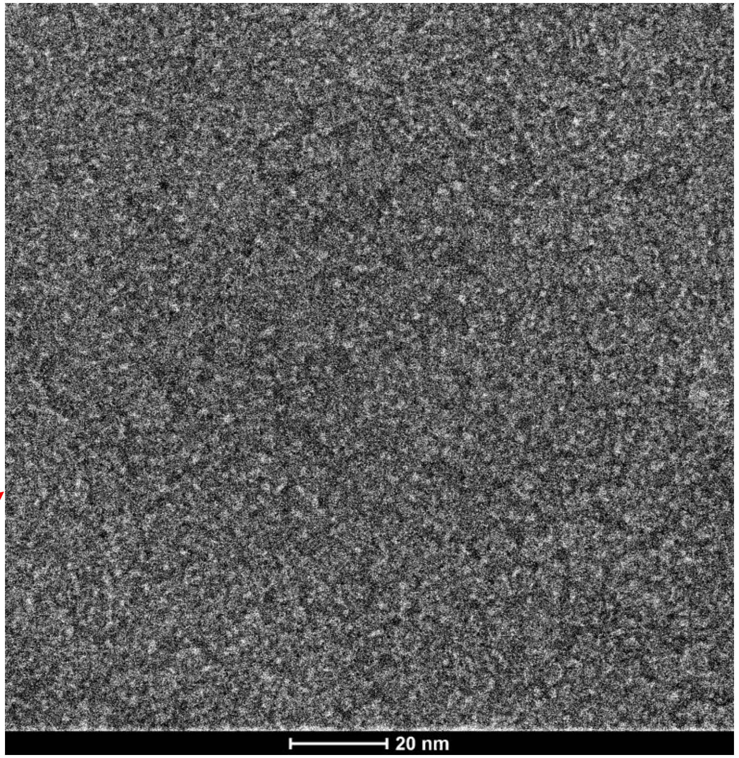
M. McGarry et al., submitted

Co-SiN_x (ϕ=0.35)

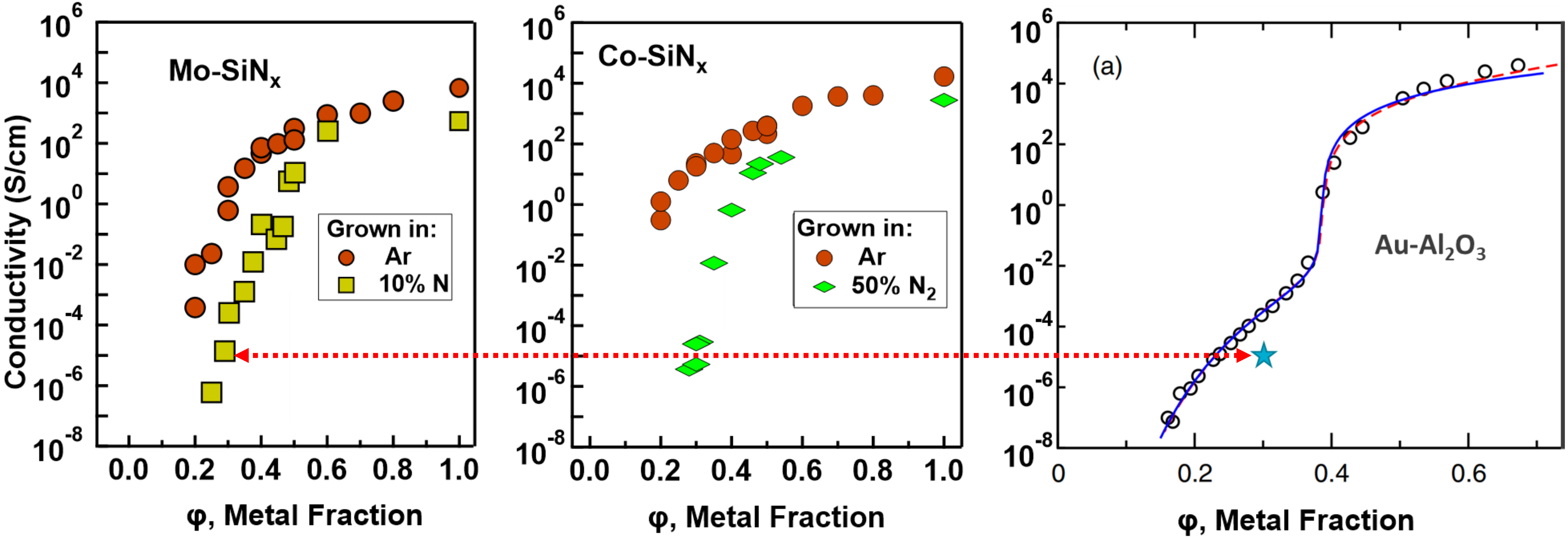
50% N_2



S.J. Gilbert et al., in progress



Significant insulator improvements when deposited N_2



M. McGarry et al., submitted

S.J. Gilbert et al., in progress

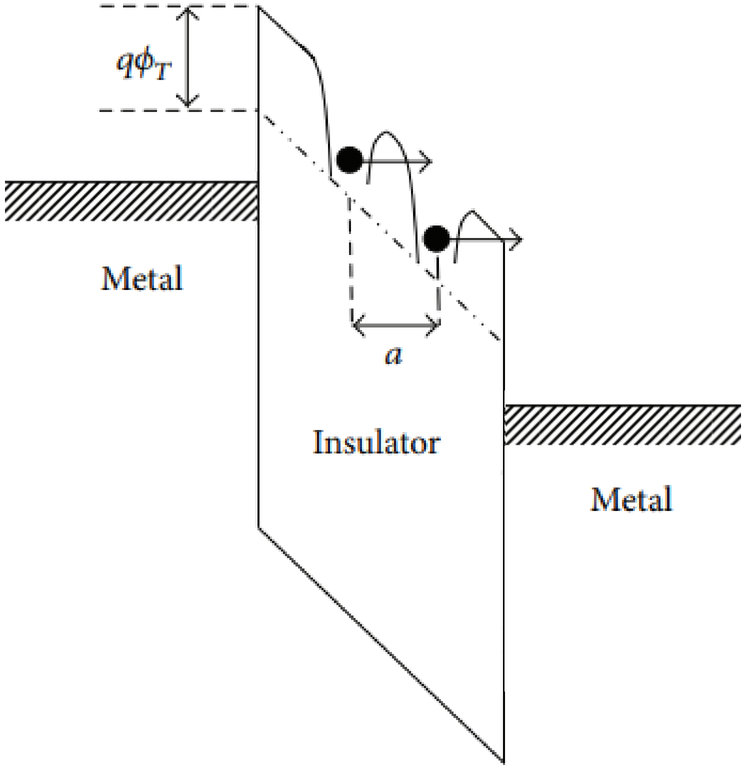
Data: Abeles et al. Adv. in Phys. **24**, 407 (1975)

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

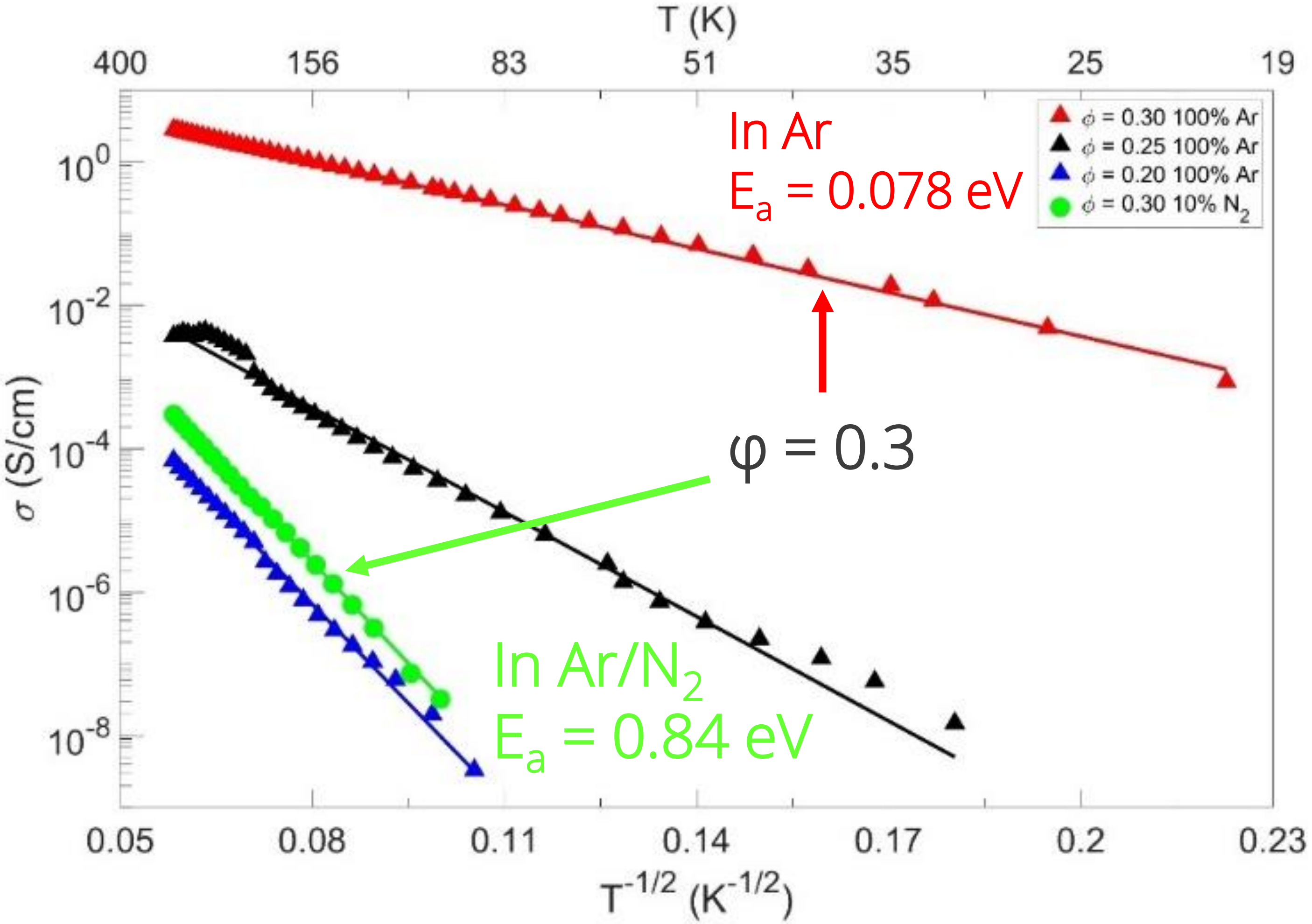
Low conductivities previously only seen with noble metals.

Deposition in N_2 greatly increases activation energy

Hopping Conduction



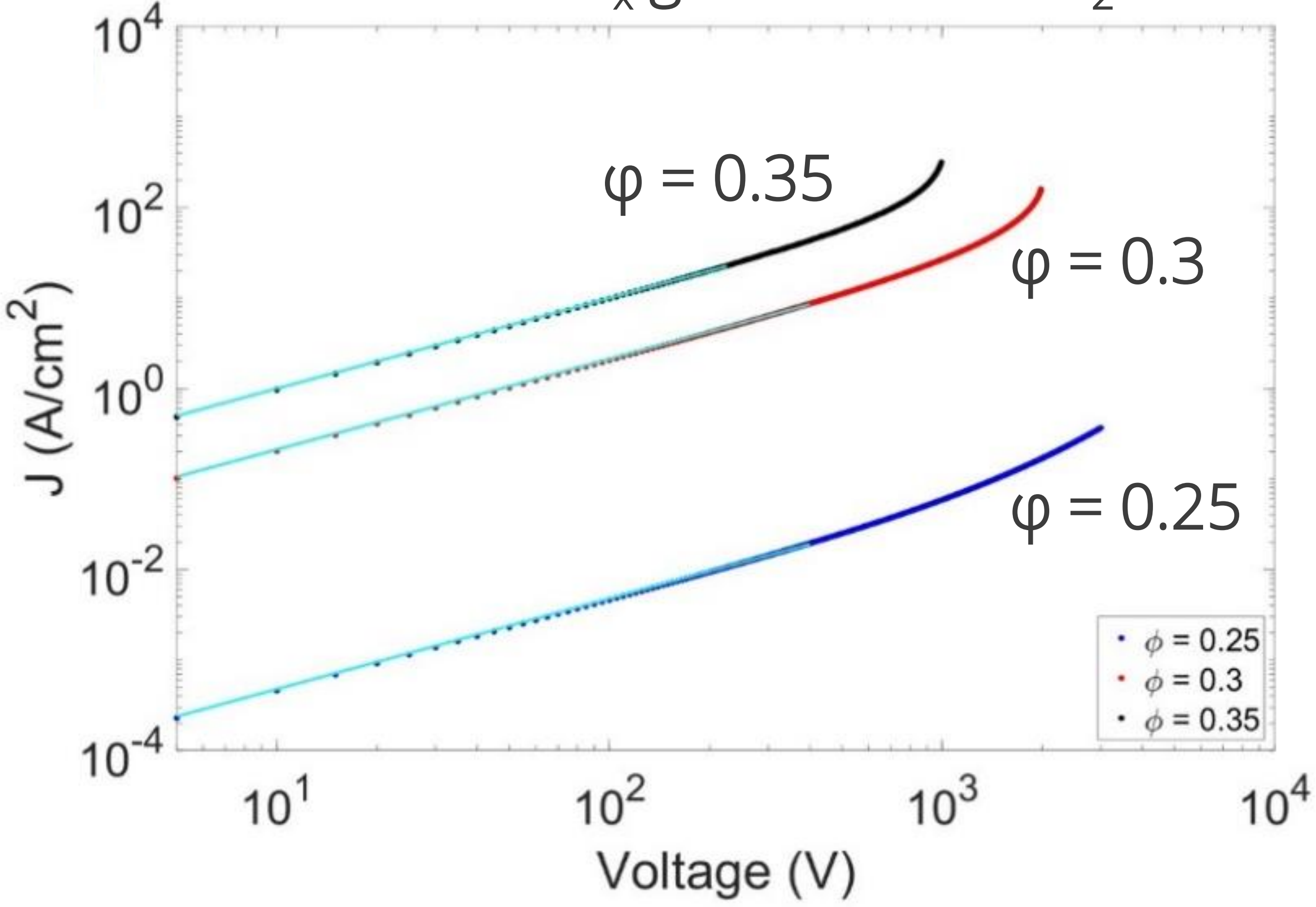
$$\sigma \propto \exp\left(-2\sqrt{E_A/k_BT}\right)$$



Fu-Chien Chiu, Advances in Materials Science and Engineering, **2014**, 578168, (2014)

Field enhanced tunneling is observed at higher electric fields

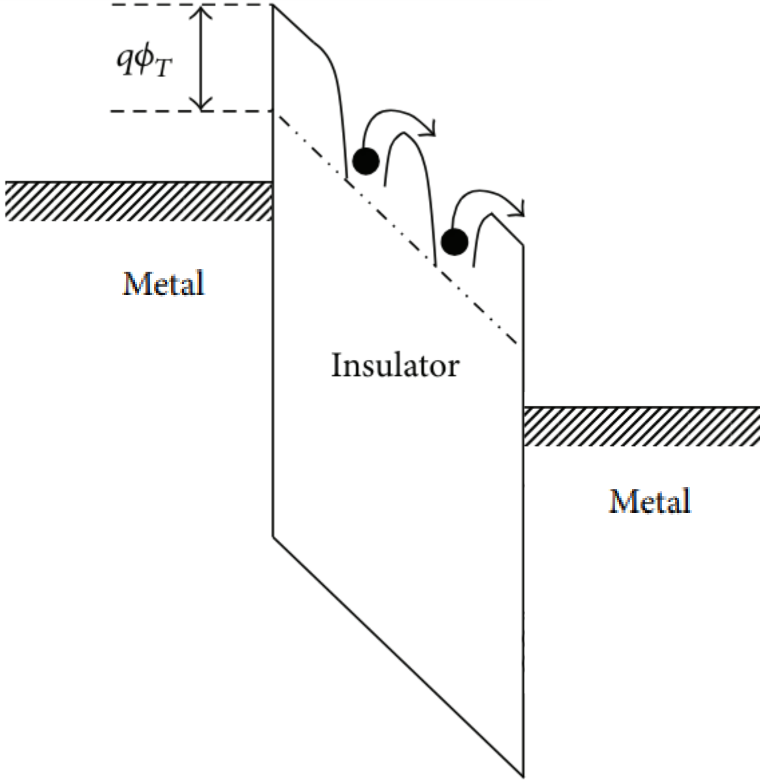
Mo-SiN_x grown in 10% N_2



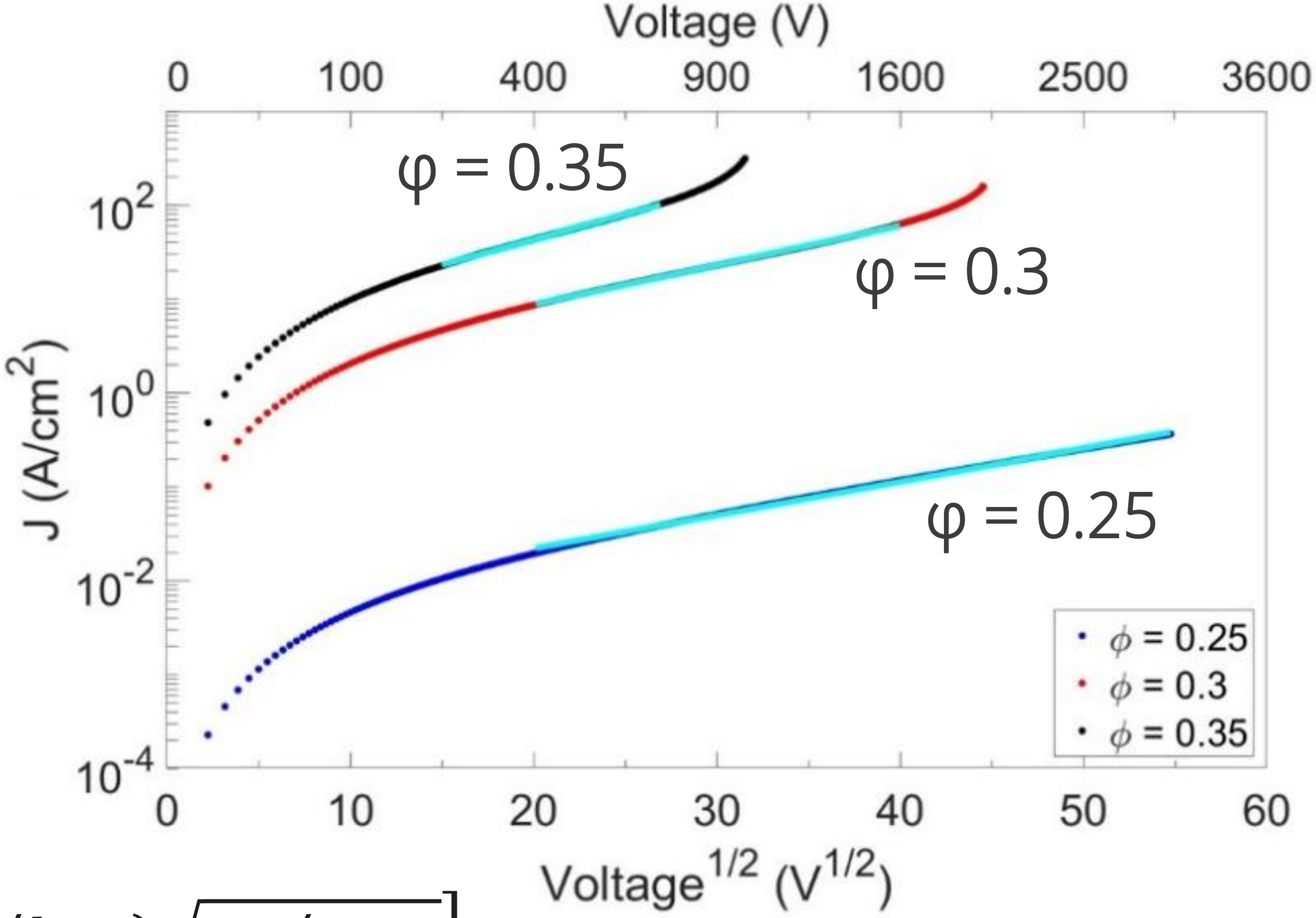
Ohmic conduction up to ~20 kV/cm

Poole-Frenkel emission for electric fields >20 kV/cm

Poole-Frenkel Emission



Mo-SiN_x grown in 10% N_2



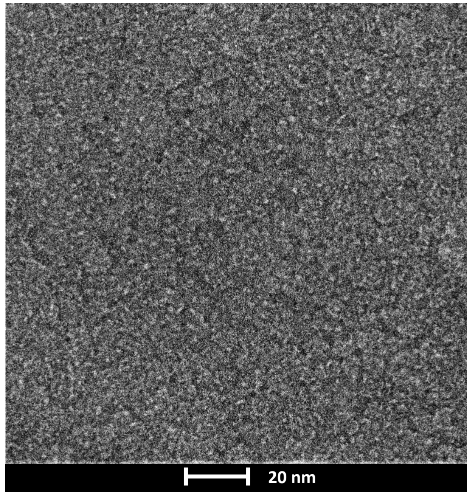
$$\sigma \propto \exp\left[(q/k_B T)\sqrt{qE/\mathcal{E}_0\mathcal{E}_r}\right]$$

Maximum voltage limited by equipment NOT material.

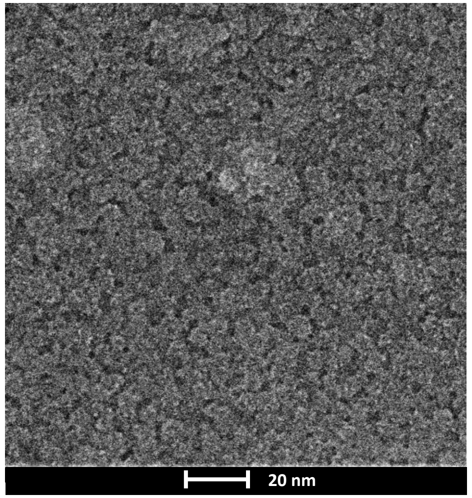
Annealing Increases Nanoparticle Size and Separation

Co-SiN$_x$ grown in 50% N$_2$ (ϕ=0.35)

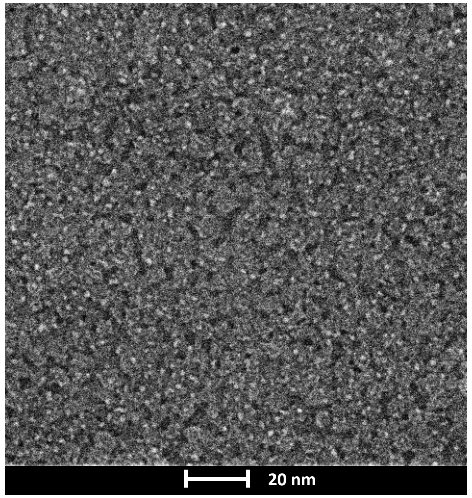
unannealed



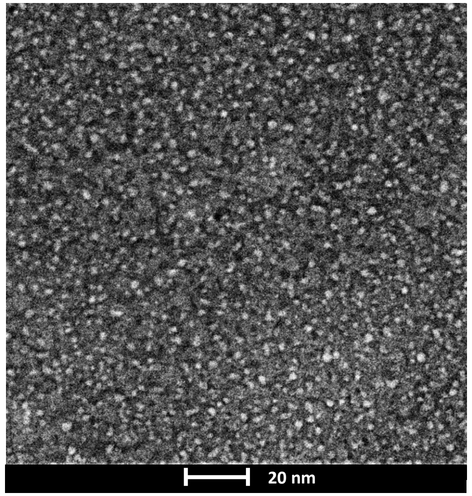
300 ^{o}C



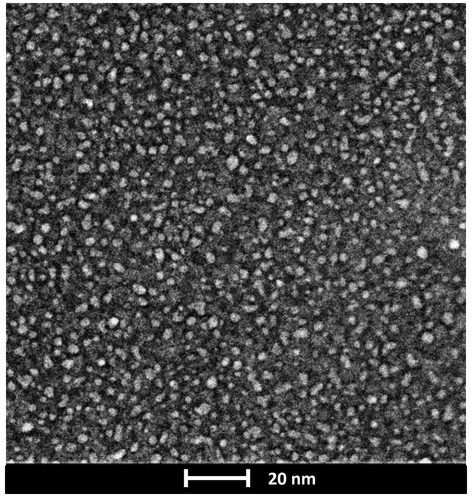
400 ^{o}C



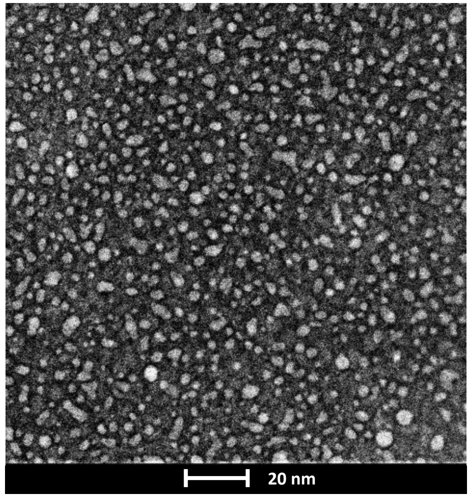
500 ^{o}C



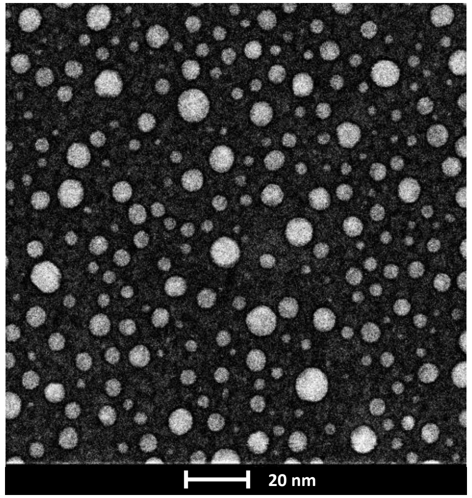
600 ^{o}C



700 ^{o}C



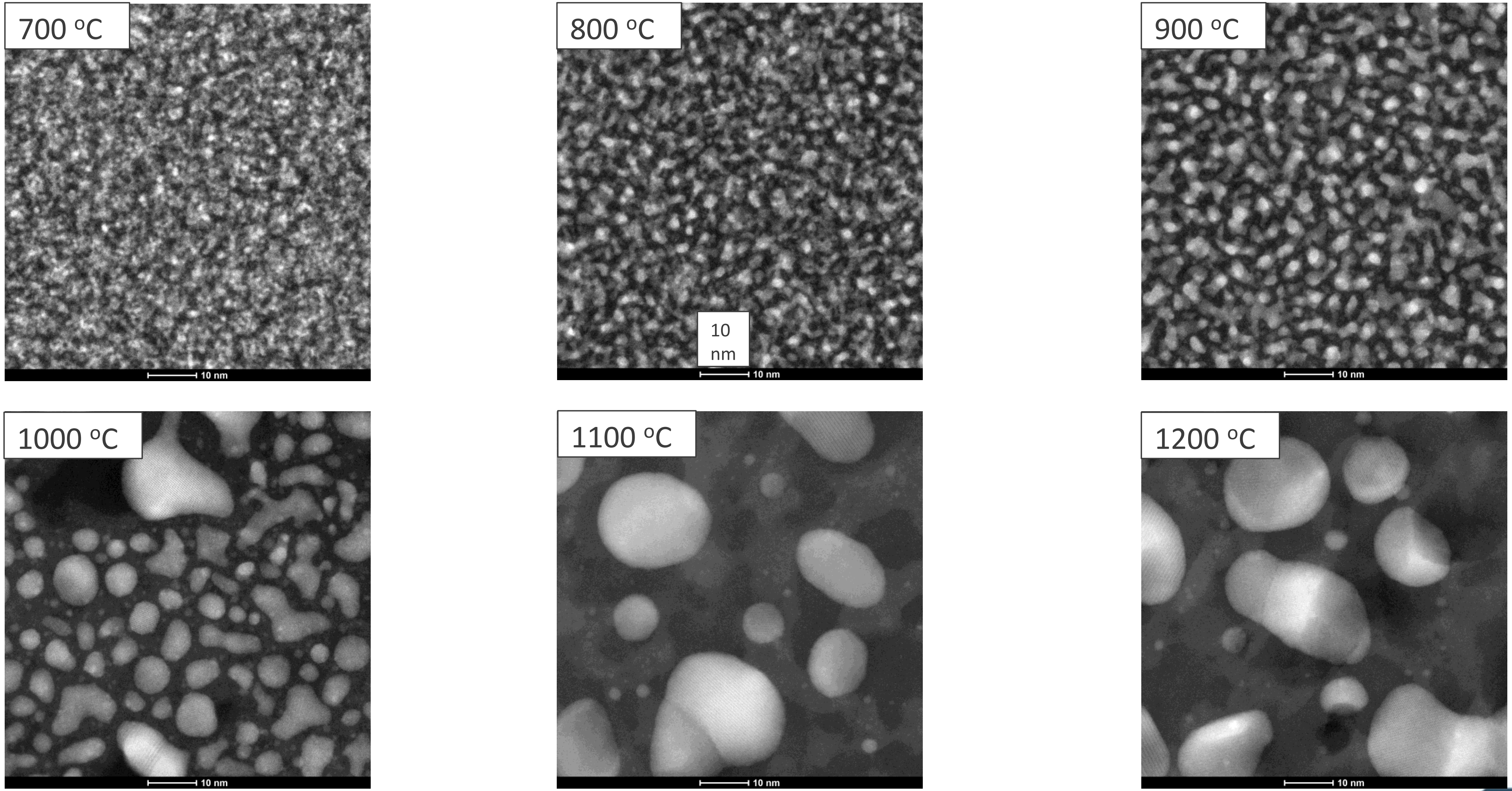
1000 ^{o}C



S.J. Gilbert et al., in progress

Mo-SiN_x is stable up to ~800 °C

Mo-SiN_x grown in 10% N_2 (ϕ=0.4)

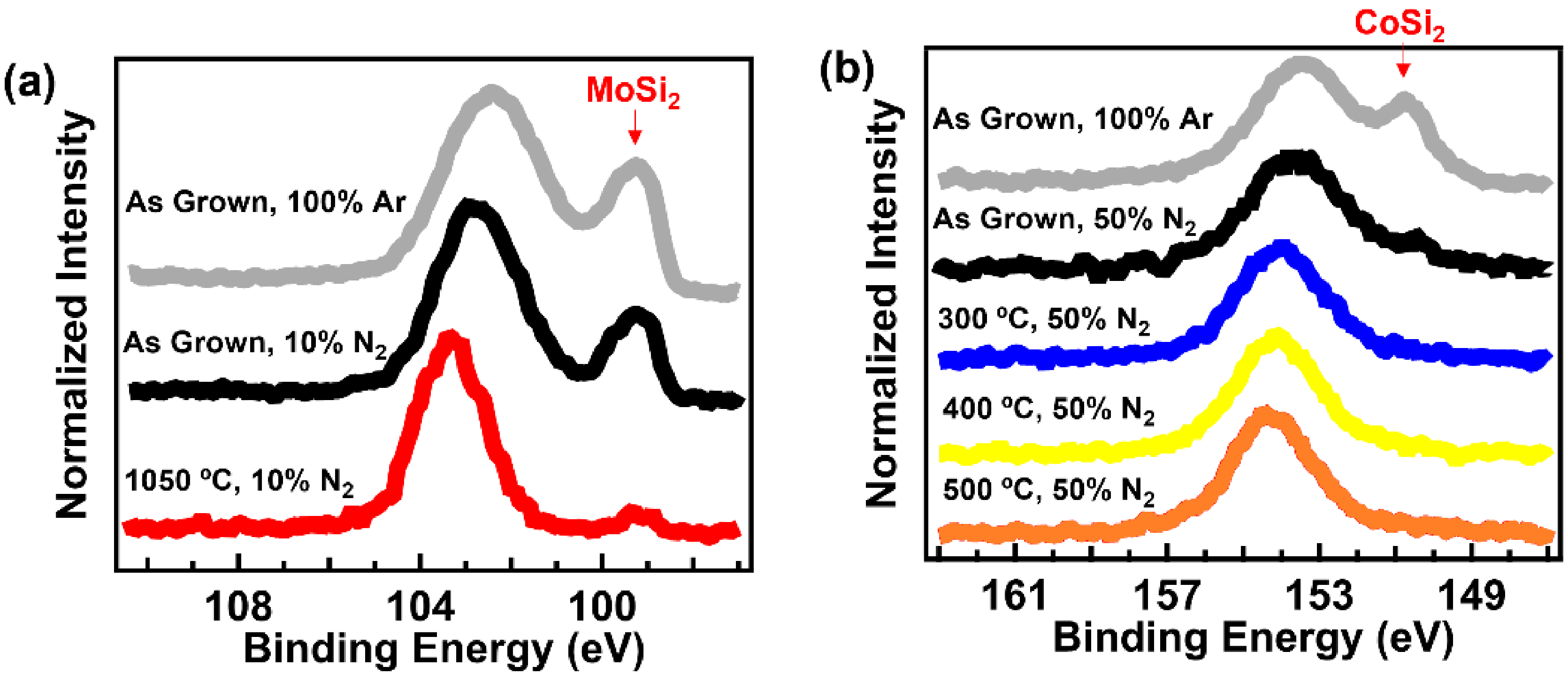


M. McGarry et al., in progress

Deposition in N_2 and Annealing Reduce Metal-Silicide Content

Mo-SiN_x Si 2p spectra

Co-SiN_x Si 2s spectra

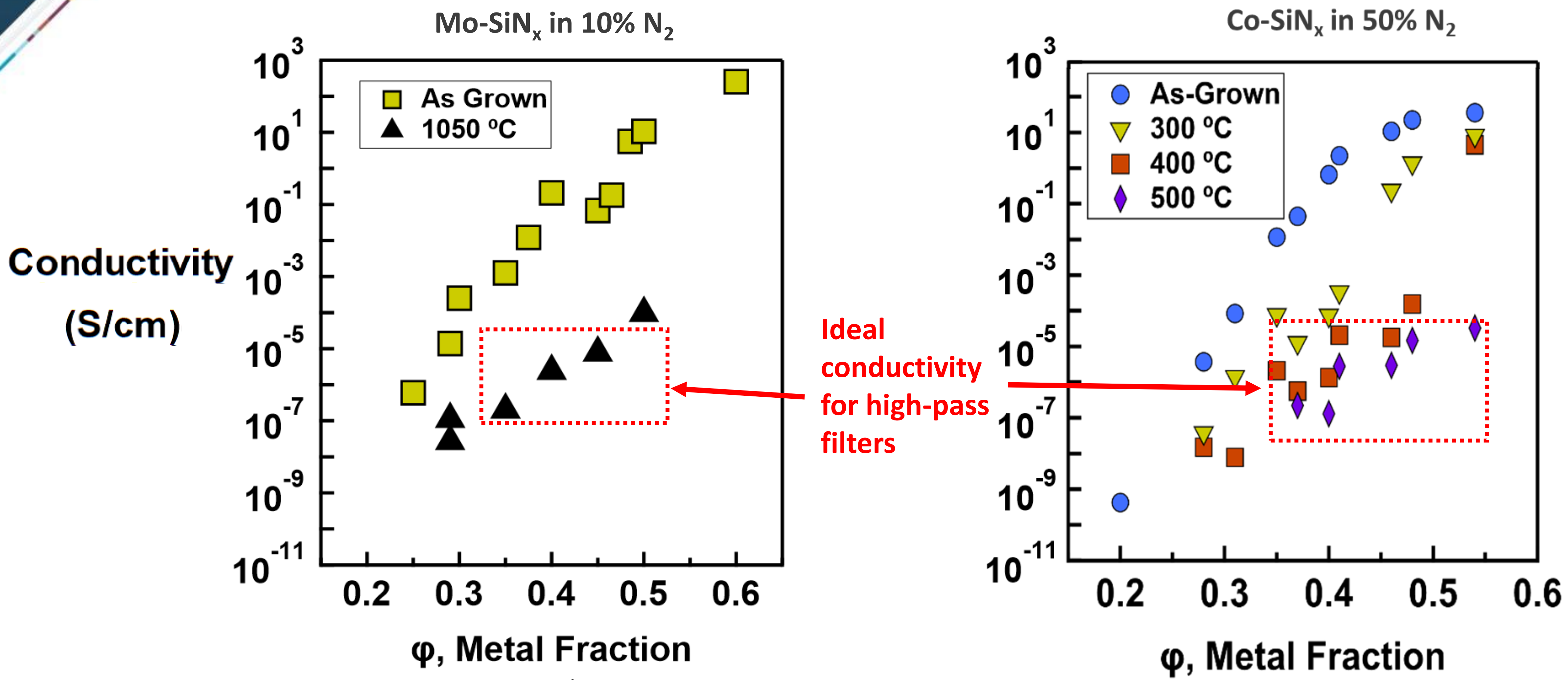


S.J. Gilbert et al., in progress

Group	Compound	$\Delta_f H$ (kJ*mol^{-1}*atom^{-1})	Ref.
Silicon nitride	Si_3N_4	-118	1
Mo-silicides	Mo_3Si	-31	2
	Mo_5Si_3	-39	3
	$MoSi_2$	-46	4
Co-silicides	Co_2Si	-41	5
	CoSi	-48	5
	$CoSi_2$	-33	5

1. P. A. G. O'Hare et al., The Journal of Chemical Thermodynamics **31** (3), 303-322 (1999).
2. I. Tomaszkiewicz et al., The Journal of Chemical Thermodynamics **28** (1), 29-42 (1996).
3. I. Tomaszkiewiczet al., The Journal of Chemical Thermodynamics **29** (1), 87-98 (1997).
4. P. A. G. O'Hare et al., The Journal of Chemical Thermodynamics **25** (11), 1333-1343 (1993).
5. D. Lexa et al., Chemistry of Materials **8** (11), 2636-2642 (1996).

Annealing further improves insulator quality.



M. McGarry et al., in progress

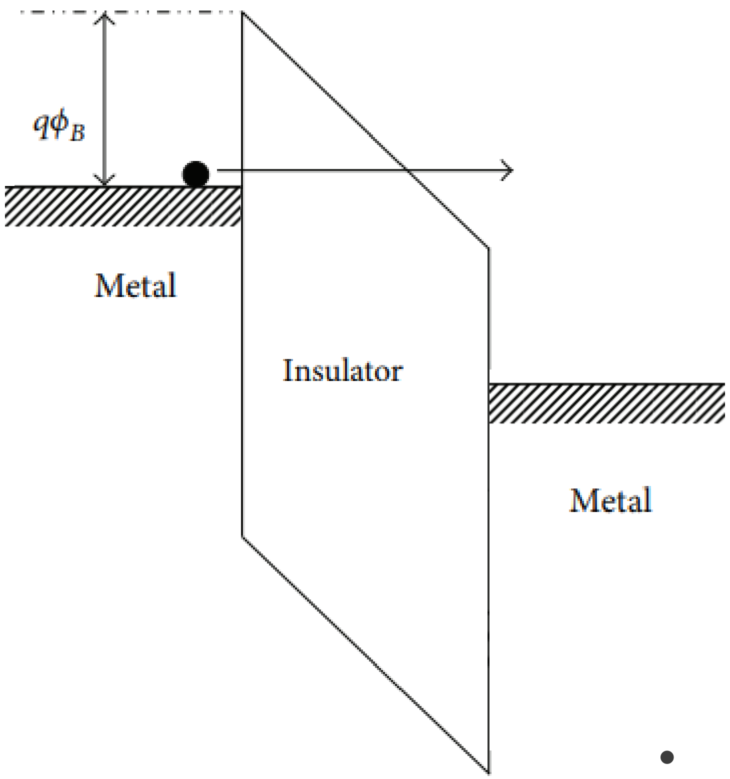
S.J. Gilbert et al., in progress

Potential protection devices with ≥ 50% metal fraction.

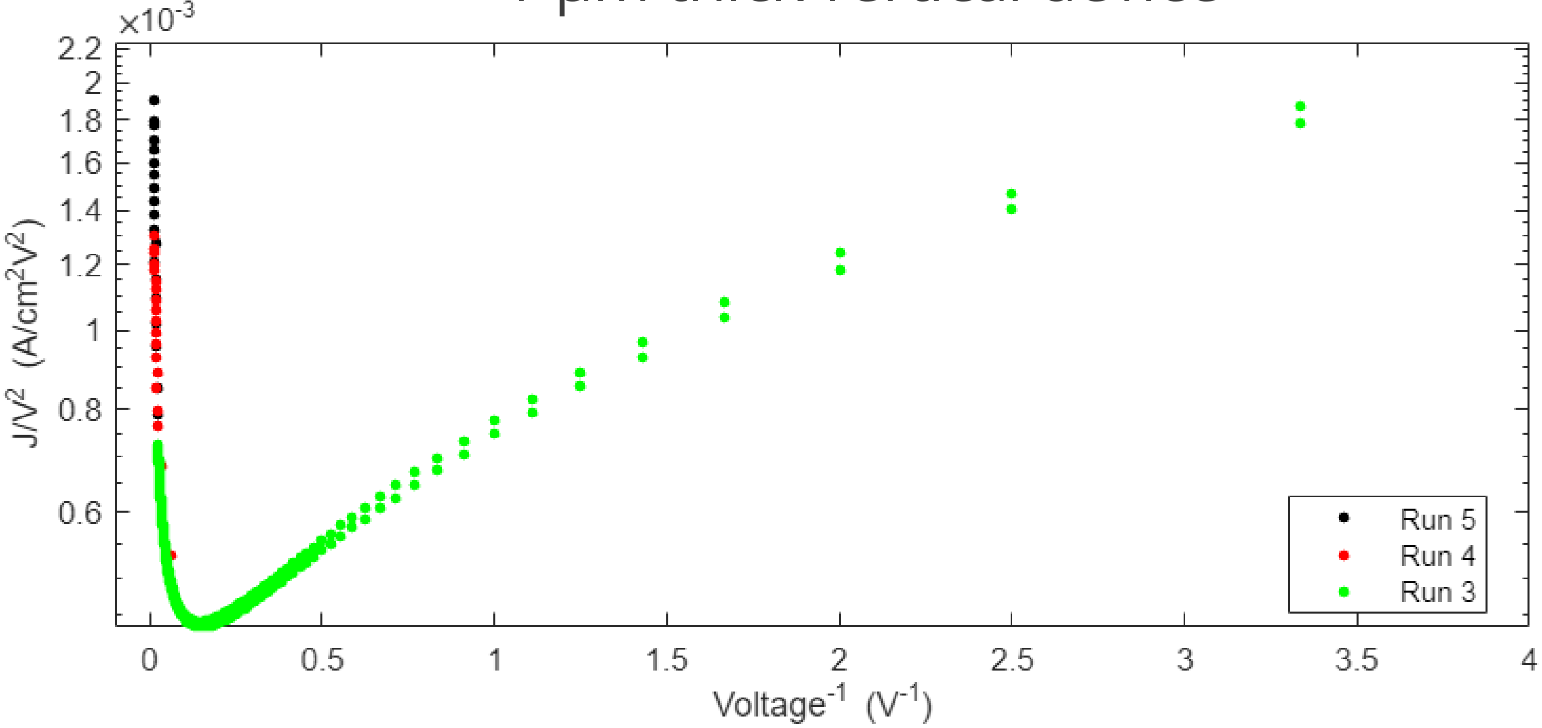
Fowler-Nordheim tunneling enhances current carrying capacity

Mo-SiN_x grown in 10% N_2
φ = 0.3, 1050 °C anneal
1 μm thick vertical device

Fowler-Nordheim Tunneling



$$\sigma \propto E^2 \exp(E_0/E)$$

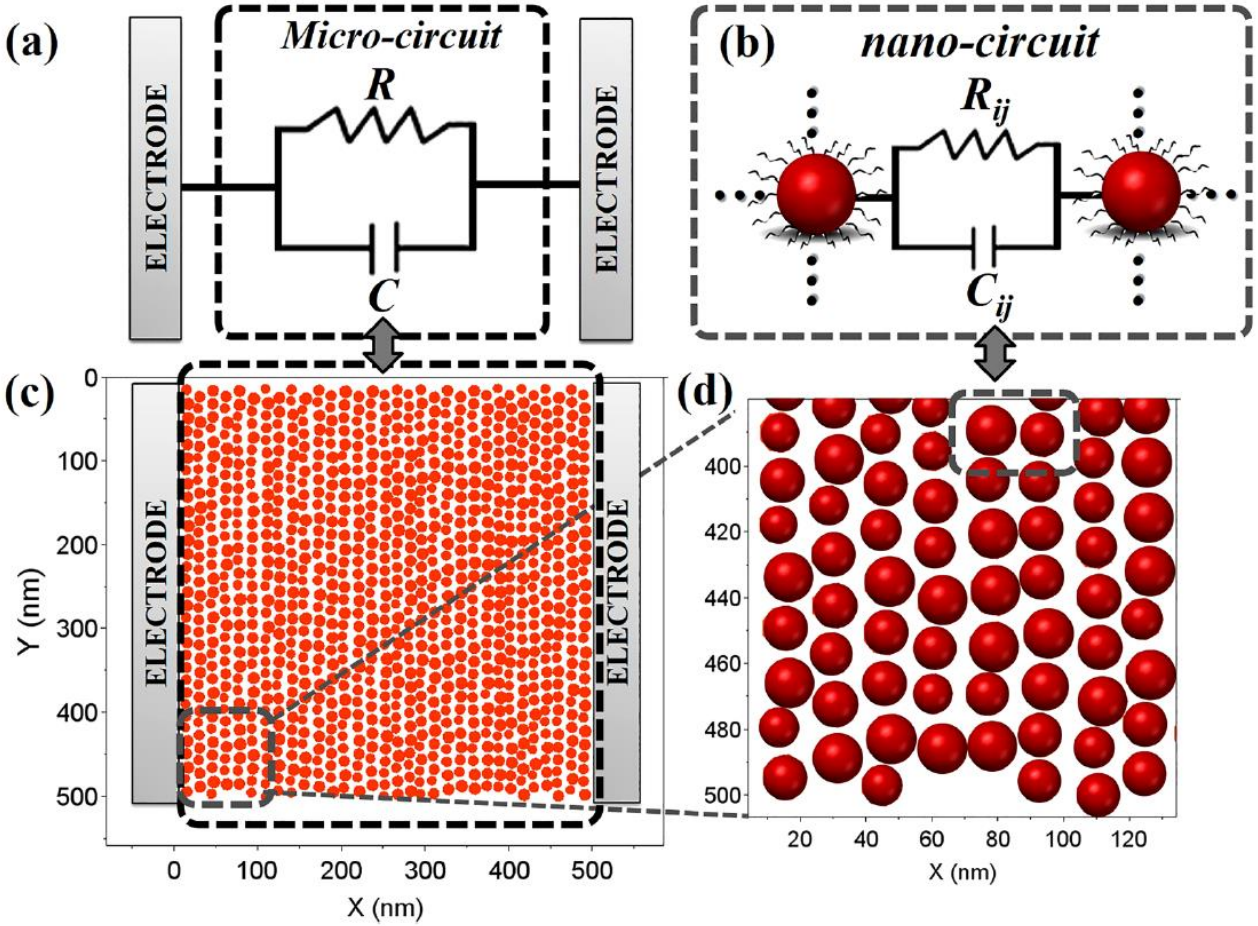


M. McGarry et al., in progress

- High breakdown strength (>0.8 MV/cm) allows for compact devices.
- Current densities measured up to 10 A/cm^2.

High frequencies also enhance GM conductivity.

Complementary tunneling and capacitive conduction paths.



L. Merle et al., J. Appl. Phys. **132** (1), 015107 (2022).

GMs follow Jonscher's universal power law

$$\sigma_{AC}'(\omega) = \sigma_{DC} + A\omega^n$$

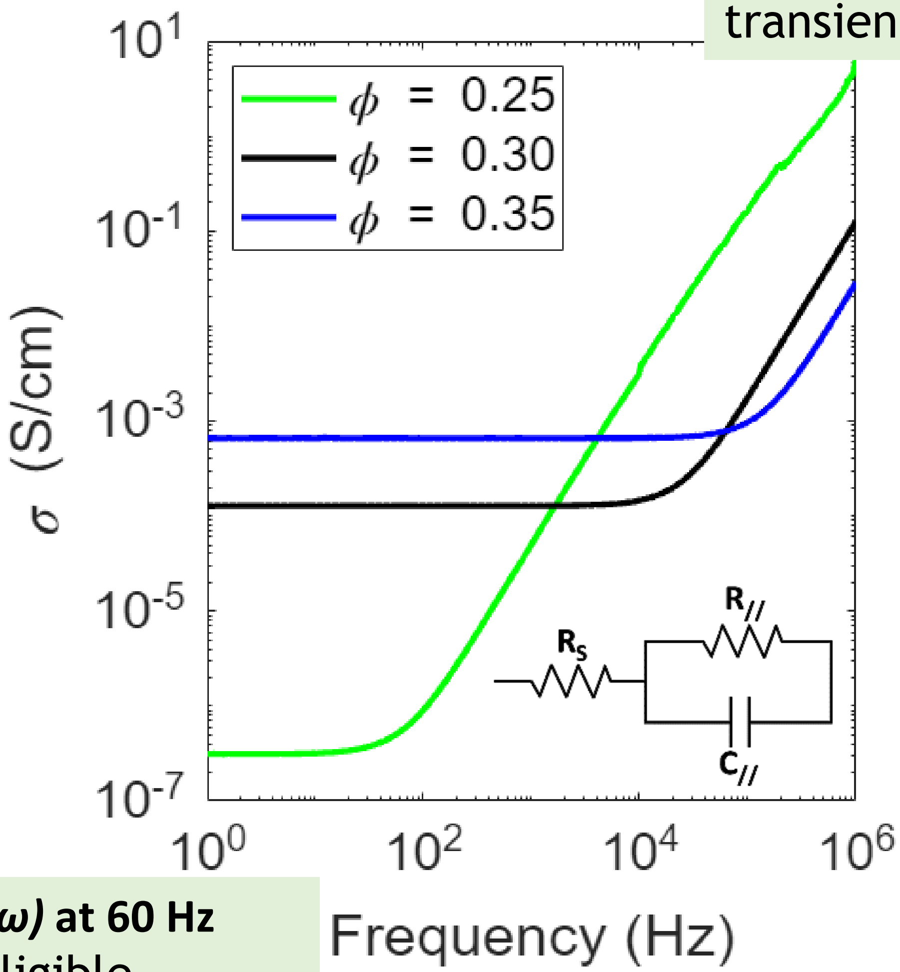
Tunneling dominates at low frequencies.

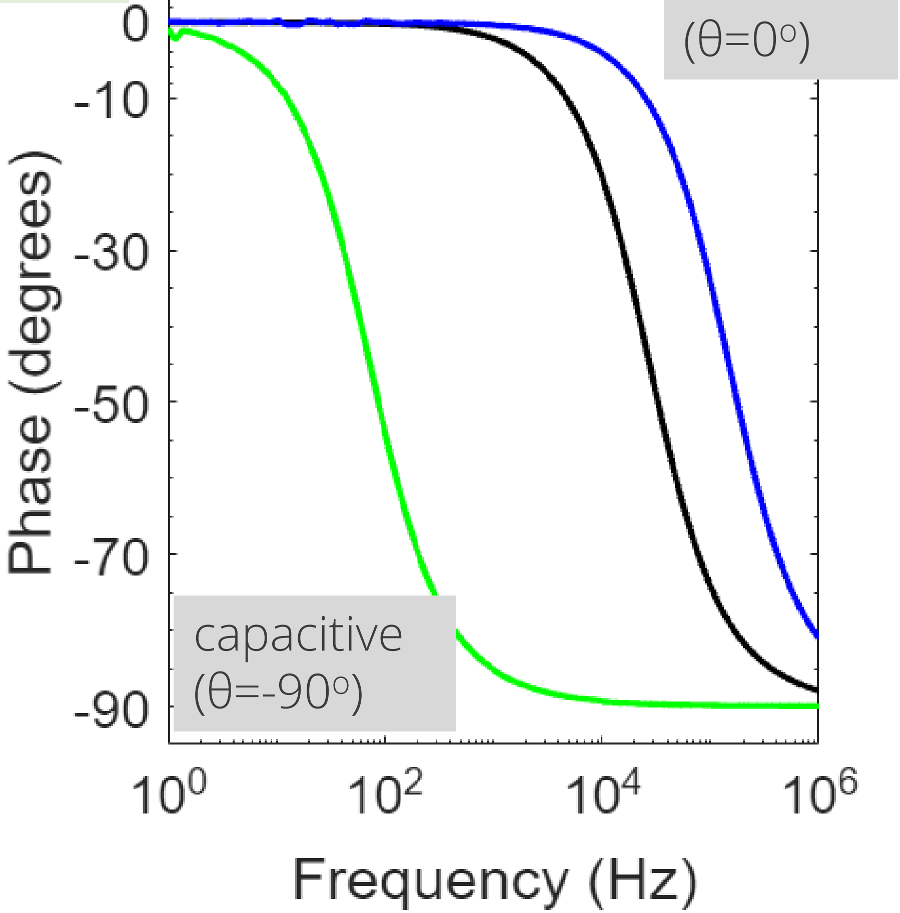
Capacitive transport dominates at high frequencies.

Material advances result in extraordinarily σ_{AC} response

Mo-SiN_x grown in 10% N_2

High *σ(ω)* at MHz
→ Shunt ns transients



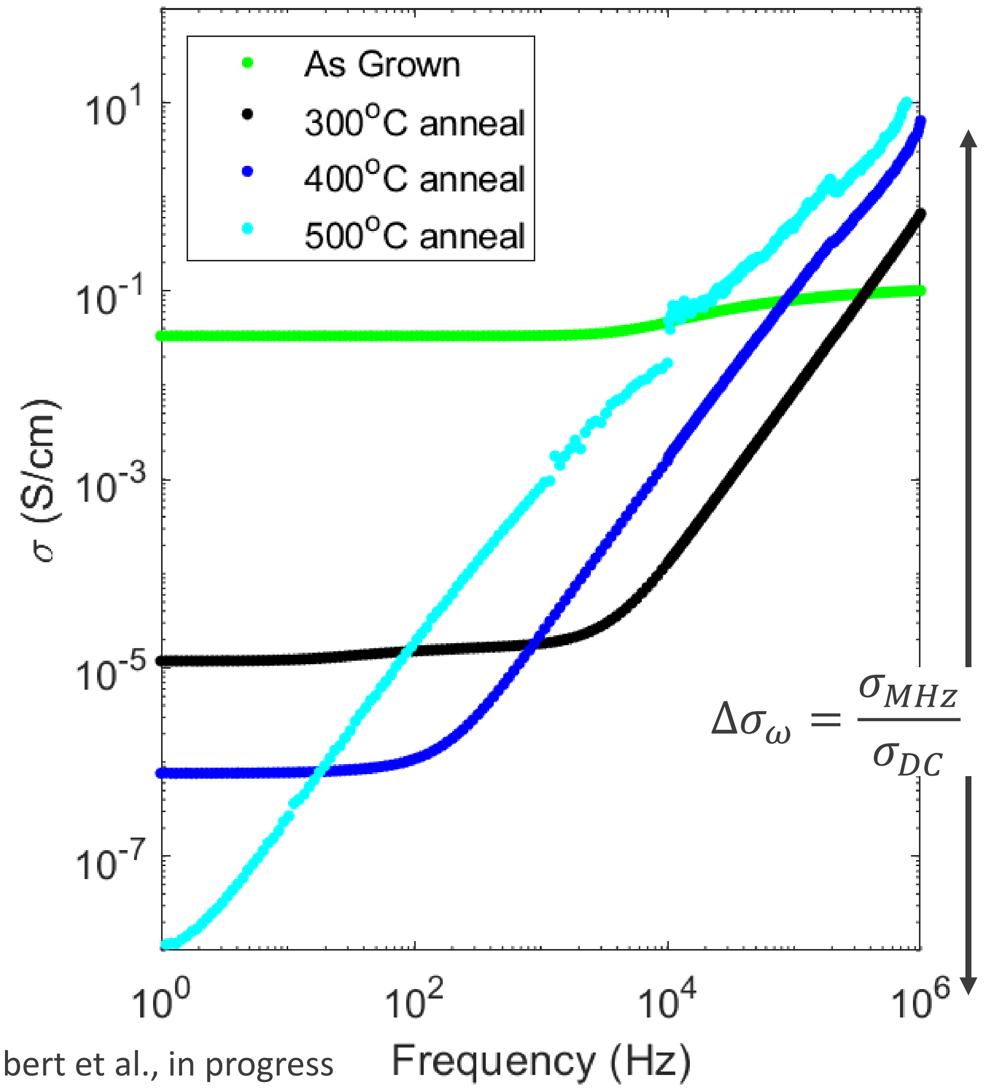


Low *σ(ω)* at 60 Hz
→ Negligible leakage current

M. McGarry et al., submitted

Material advances result in extraordinarily σ_{AC} response

Co-SiN$_x$, grown in 50% N_2, φ = 0.4



S.J. Gilbert et al., in progress

GM	Annealing	φ	$\Delta\sigma_\omega$
Literature			
Pd-ZrO_2 [1]	As Grown	0.28	50
$(FeCoZr)_x(PZT)_{(100-x)}$ [2]	As Grown	0.52	100
Pt-SiO_2 [3]	As Grown	0.3-0.6	$10^3 – 10^4$
This LDRD			
Mo-SiN$_x$, 10% N_2	As Grown	0.35	40
Mo-SiN$_x$, 10% N_2	As Grown	0.30	10^3
Mo-SiN$_x$, 10% N_2	As Grown	0.25	10^7
Mo-SiN$_x$, 10% N_2	1050 °C	0.29	10^8
Co-SiN$_x$, 50% N_2	As Grown	0.4	<10
Co-SiN$_x$, 50% N_2	300 °C	0.4	10^5
Co-SiN$_x$, 50% N_2	400 °C	0.4	10^7
Co-SiN$_x$, 50% N_2	500 °C	0.4	10^9

1. H. Bakkali et al., Sci. Rep. **6**, 29676 (2016).
2. O. Boiko et al., AIP Advances **12** (2), 025306 (2022).
3. N. Moyo and K. Leaver, J. Phys. D: Appl. Phys. **13** (8), 1511 (1980).

Conclusion: Granular Metals are promising for nanosecond high voltage transient protection

- ☑ compact — >1 MV/cm breakdown strength
- ☑ insulating at 60 Hz and low electric fields — Conductivities of 10^{-5}-10^{-7} S/cm
- ☑ high thermal stability — Mo-SiN_x stable to ~800 °C
- ☑ conducting for 1 GHz voltage spikes — >10^6 conductivity increase at 1 MHz
- ? ❑ large current carrying capacity (>1 kA/cm^2) — Coupled high frequency/electric-field measurements needed.

sjgilbe@sandia.gov