Metallization & Interconnection WORKSHOP

Screen Printable Fire Through Nickel Contacts for Crystalline Silicon Solar Cell

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Outline

- **Motivation**
- **Approach**
  - -Paste Preparation
  - -Wafer Preparation
  - -Printing
- **Results**
  - -Electrical Performance
  - -Microstructural Analysis
- **Future Work and Conclusion**

Motivation: Why is Ag problematic?

The total supply of Ag demand is about to lack meeting the demand!

Environmental impact of Ag is greater than the alternatives.

Alternatives such as nickel are evenly distributed around.

Silver Supply/Demand Summary [1]					
	2012	**2016**	**2020**	**2022**	**2030**
Total Supply (MOz)	1,008	1,046.9	953.0	1,030.3	1075.6
Electrical and Electronics	270.9	308.9	304.1	353.3	435.7
Total Industrial	445.2	475.3	464.9	539.6	628.5
Jewellery/Bar/Coin	439.9	400.4	354.8	481.0	524.2
Photovoltaics	55.0	93.7	101.0	127.0	251.2
Total Demand	978.8	979.4	880	1,101.8	1252.2
Price (per ounce)		$17.17	$20.69	$21.76	$80-$120

[1] The Silver Institute
[2] Metal Focus

Motivation: What are the alternatives?

	28 Ni Nickel	29 Cu Copper	47 Ag Silver
Price (per kg)	$24	$8	$808
Conductivity (S/m)	14.9×10^6	59.6×10^6	62.1×10^6
Metal work function (eV)	5.02 – 5.43	4.64 - 4.82	4.69 - 4.85
Adhesion	Best	Good	Good
Environmental impact	Low	Medium	High

Motivation: Why Ni over Cu?

Ni has higher resistance to **oxidation** compared to Cu

Ni has higher resistance to **humidity (corrosion)** compared to Cu

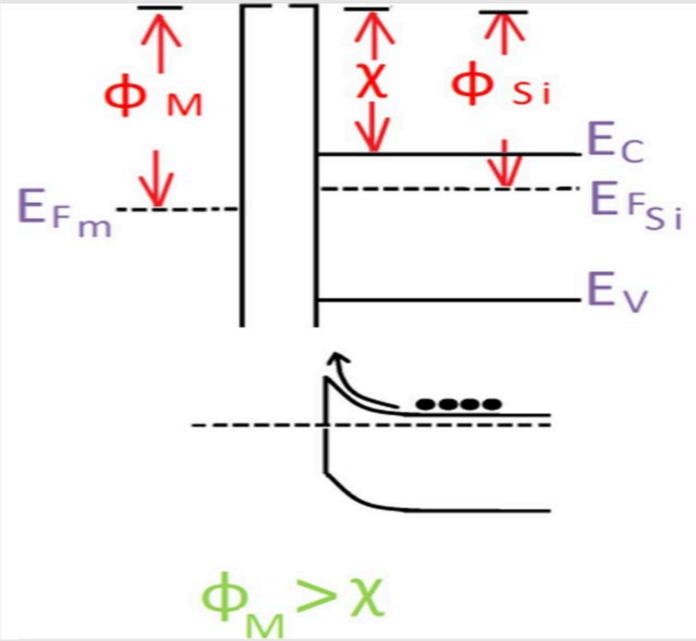
Ni has better **adhesion** to Si than Cu

Ni has **no diffusion** into Si during high temperatures like Cu

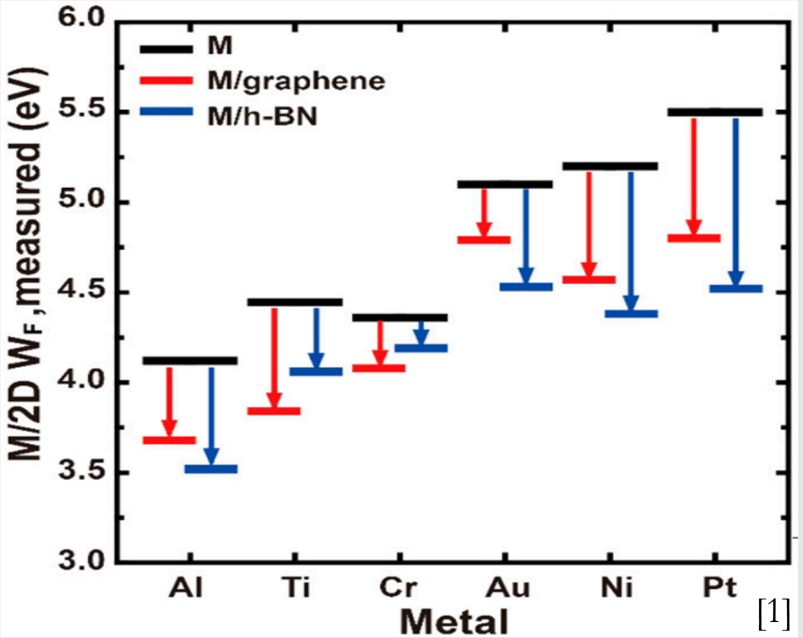
Approach: Requirements for a Ni based contacts

1- Good ohmic contact formation

- Ni has a work function of over 5 eV
- c-Si has the electron affinity of 4.05eV



- To avoid Schottky contact formation, the metal work function is tuned

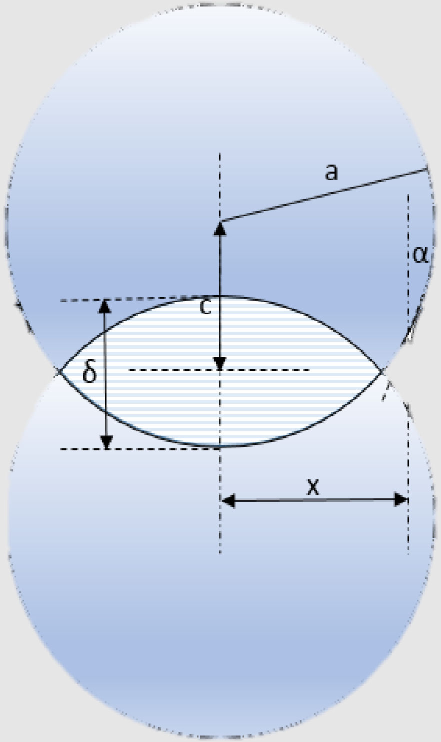


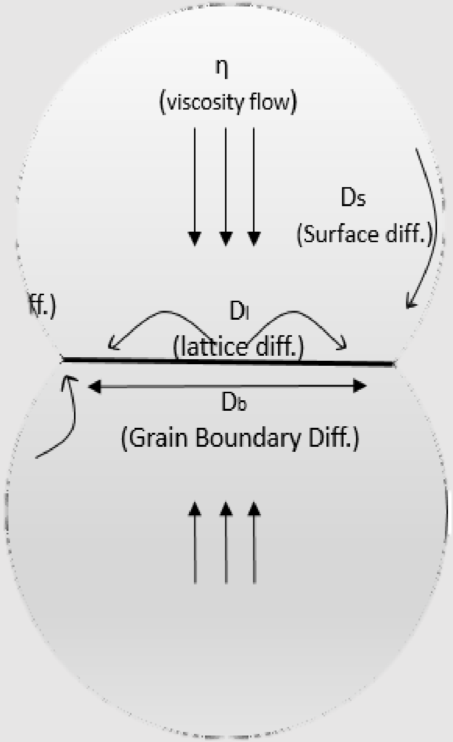
- There's a flow of electrons from 2D material to the metal that lowers the metal work function

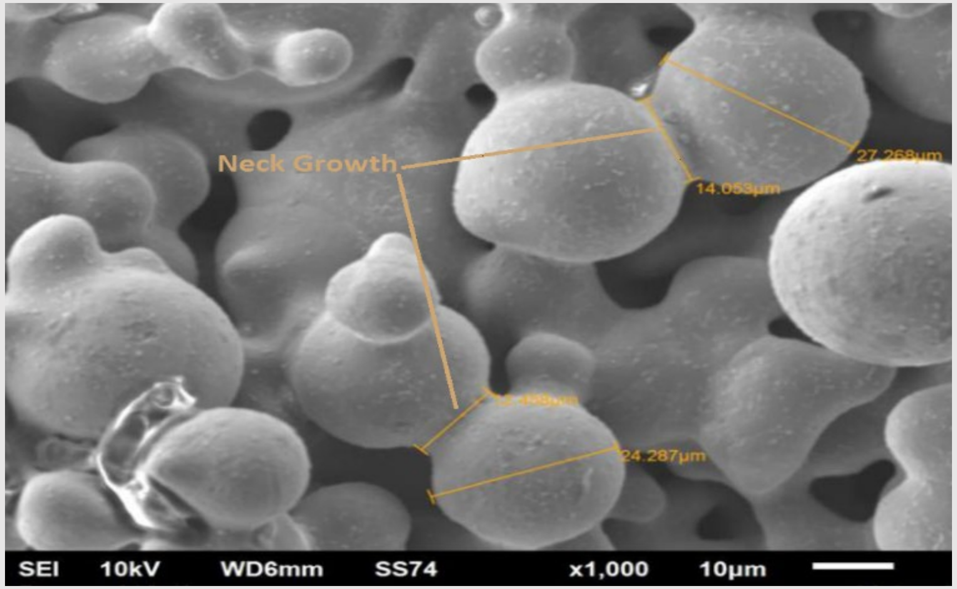
[1] Nano Lett. 2018, 18, 8, 4878–4884

Approach: Requirements for a Ni based contacts

2- Low series resistance - finger resistance - sintering







$$\Delta V \propto \frac{t \cdot T}{r^3}$$

r ↑ → ΔV ↓↓↓

t ↑ → ΔV ↑

T ↑ → ΔV ↑

ΔV: shrinkage volume
r : radius of Ag particles
t : time
T : temperature
Dv: diffusion coefficient

Approach: Requirements for a Ni based contacts

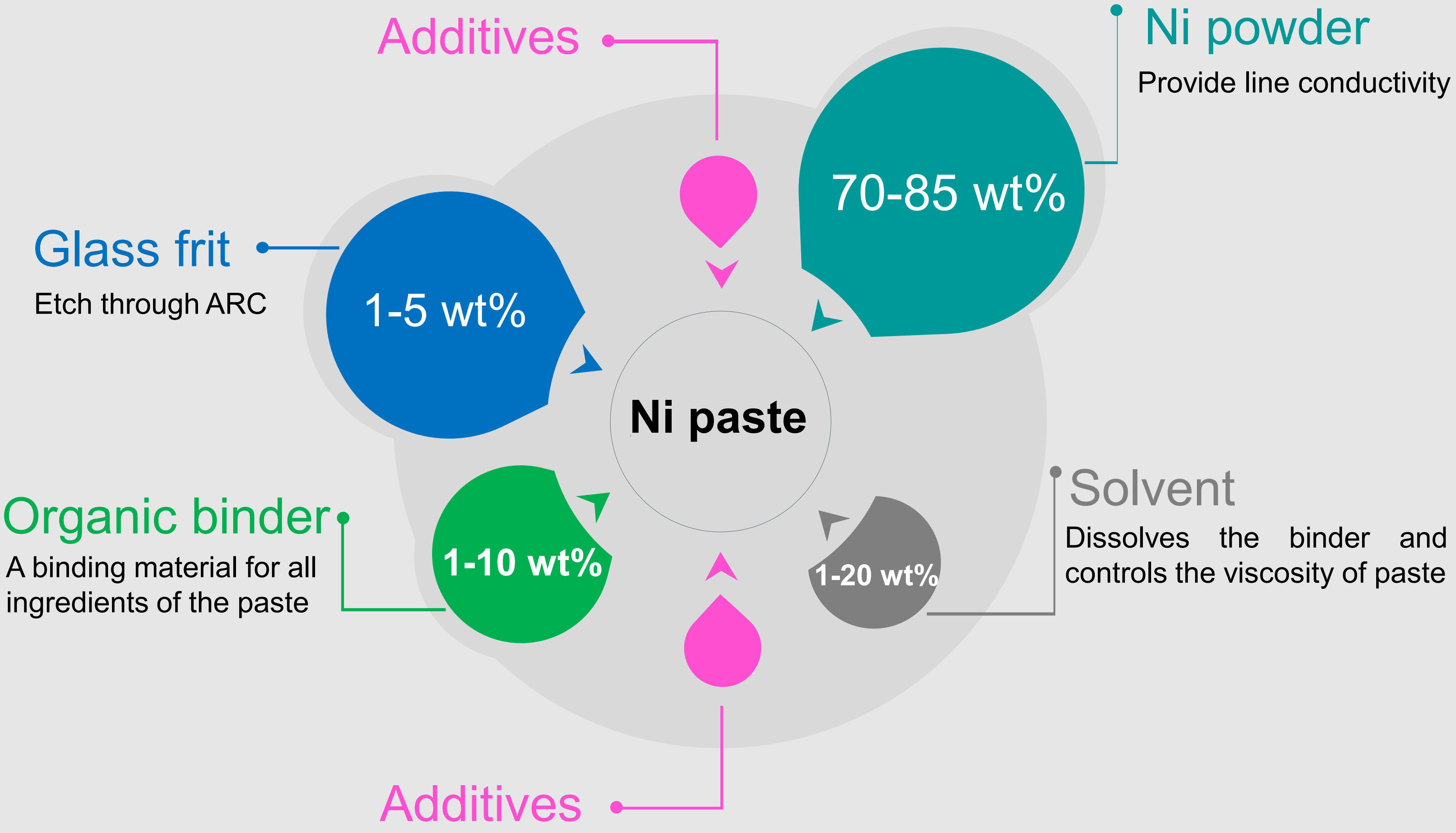
3- Low diffusivity into Si

- Ni atom clusters are bigger than Cu which doesn’t allow moving through interstitial sites in the Si lattice
- Ni has moderate solubility in Si compared to Cu that has high solubility
- The binding energy between Ni and Si is stronger than Cu/Si

4- Adhesion

- Relatively strong binding energy between Ni and Si provides good adhesion

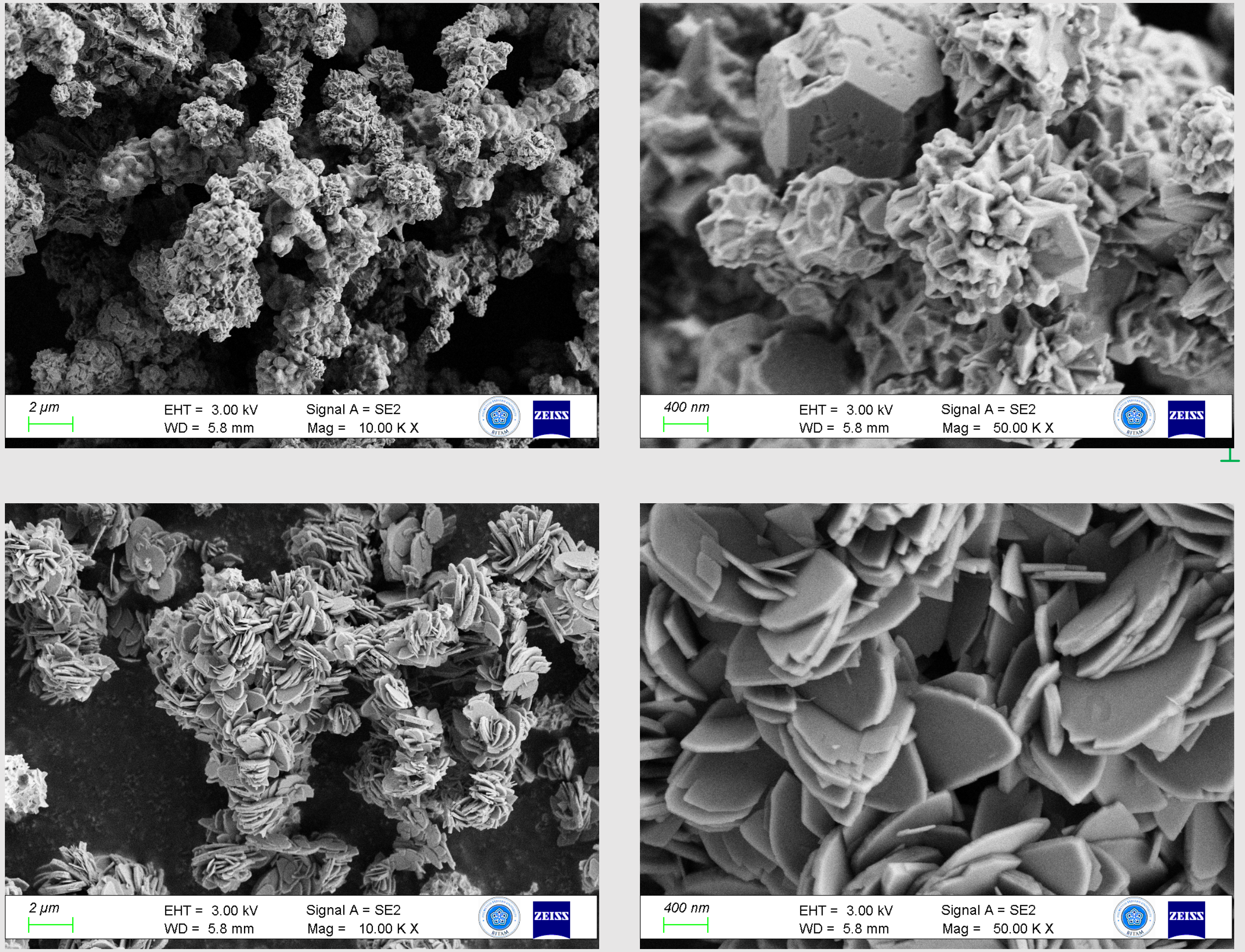
Approach: Paste Preparation



Approach: Metal Powder

- The metal particle size is below 1μm
- To increase the surface energy of the Ni particles, the surface is treated

	Diameter at 10.00 %	Diameter at 50.00 %	Diameter at 90.00 %
Min.	0.112	0.463	1.402
Max	0.113	0.470	1.425
Mean	0.112	0.466	1.414
Standard deviation	0.001	0.004	0.011
CV	0.511	0.758	0.806
	0.113	0.470	1.425
	0.112	0.466	1.414
	0.112	0.463	1.402



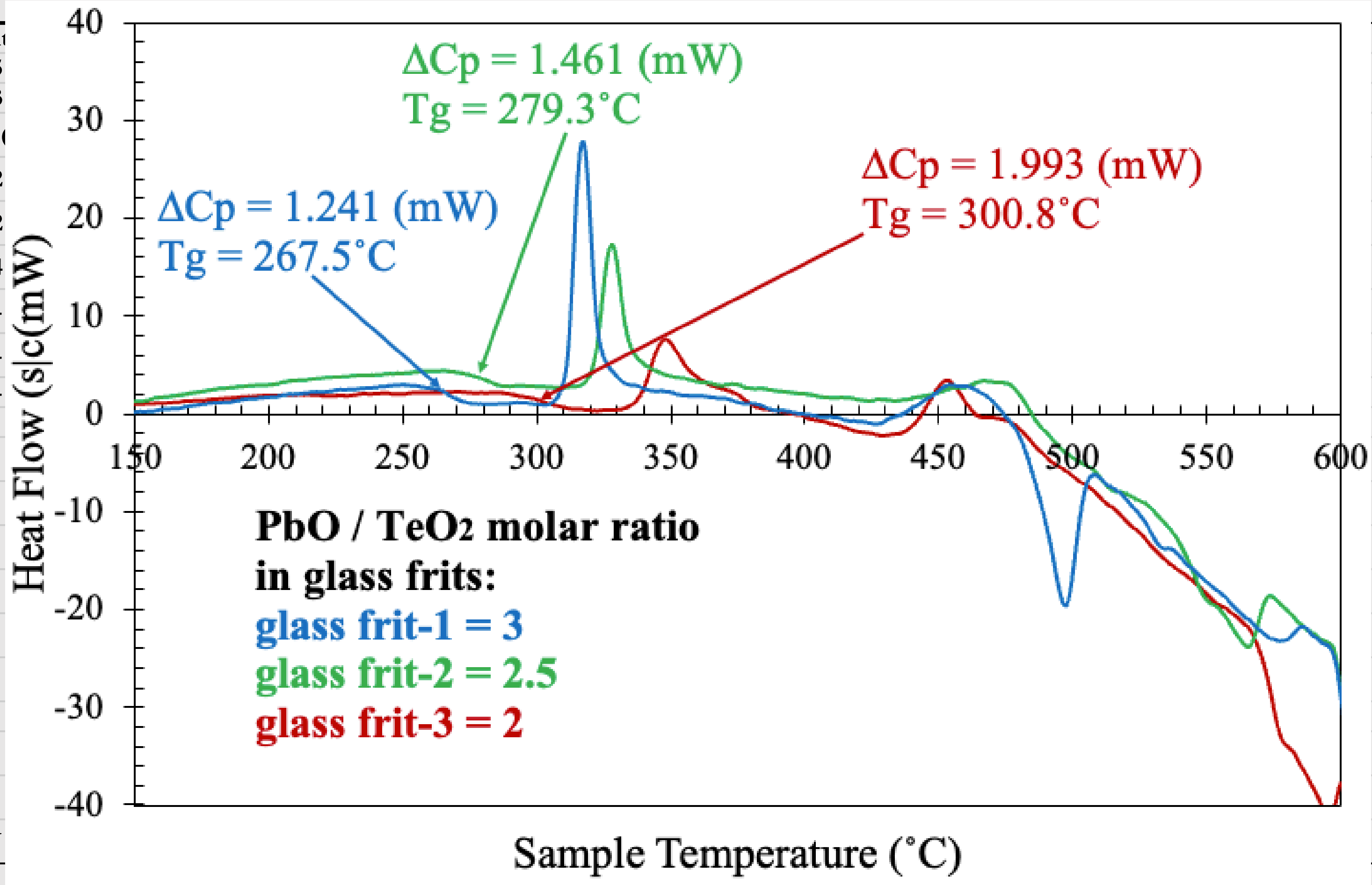
Ni Powder

Surface treated Ni

Approach: Glass Frit

Cam Frit	Tg	PbO	SiO2	Al2O3	TeO2	B2O3	Bi2O3	ZnO	MgO	WO3	Total
gf-453010-5 (1)		45%	30%	10%	5%	3%	3%	2%	2%		100%
gf-303520-3 (2)		30%	35%	20%	5%	5%	5%				100%
gf-552520 (3)	215,42 C	55%	25%	20%							100%
gf-404505-2 (4)	216,96 C	40%	45%	5%		6%		4%			100%
gf-355005-2 (5)	223,11 C	35%	50%	5%		6%		4%			100%
gf-000805-4 (6)	215,52 C		8%	5%	40%	6%	33%	8%			100%
gf-001005-4 (7)	189,1 C		10%	5%	45%	10%	25%	5%			100%
gf-201005-4 (8)	174,81 C	20%	10%	5%	25%	10%	25%	5%			100%
gf-601005-4 (9)		60%	10%	5%	10%	5%	5%	5%			100%
gf-600510-4 (10)		60%	5%	10%	5%	5%	10%	5%			100%
SB-1	300,8 C	40%	5%		20%	10%	15%	10%			100%
SB-2	279,34 C	50%			20%	10%	10%	10%			100%
SB-3	267,54 C	60%			20%	10%		10%			100%
gf-1	279,29 C	60%	10%	5%	10%	5%	5%	5%			100%
gf-2	258,30 C	60%	5%	10%	5%	5%	10%	5%			100%
gf-3	241,73 C		2%	2%	5%	20%	35%	36%			100%
gf-4					65%		15%	20%			100%
gf-5	268,61 C	24,34%	15,07%	0,89%	45,39%		8,36%	5,56%		0,39%	100%
gf-6	284,86 C	25,28%	15,66%	0,92%	41,25%		10,70%	5,78%		0,41%	100%
gf-YTU	273,97 C										0%

Approach: Glass Frit



Cam Frit	WO3	Total
gf-453010-5		100%
gf-303520-3		100%
gf-552520 (		100%
gf-404505-2		100%
gf-355005-2		100%
gf-000805-4		100%
gf-001005-4		100%
gf-201005-4		100%
gf-601005-4		100%
gf-600510-4		100%
SB-1		100%
SB-2		100%
SB-3		100%
gf-1		100%
gf-2		100%
gf-3		100%
gf-4		100%
gf-5	0,39%	100%
gf-6	0,41%	100%
gf-YTU		0%

- The resistance of the glass frit is in the range of 10^{-8} Ω·cm at room temperature!

Approach: Organic Vehicle

For the Organic vehicle:

- As solvents: Terpineol, Texanol and Butyl Butyrate
- As binders: Ethyl Cellulose or PVP
- As thixotropic agents: Castor Oil or Polyamide Wax
- As surfactants: Sorbitan Triolate

5.5 < Thixotropic index < 9.0

DVNXRVTJG 2.1.8.3-9 **VISCOSITY DATA REPORT** **17/01/23**

SAMPLE RUN INFORMATION

Test Start: 17/01/23 16:35 | Test End: 17/01/23 16:35 | Tester: Administrator
Instrument: RV (1.000000) | S/N: 86036486 | Model: DVNXRVTJG | FWV: 2.1.8.3-9
Spindle RV-06 (6) | S/N: 0 | SMC: 100.000 | SRC: 0.000 | YMC: 0.000
Global Limits: None | Temperature Offset: None | Temperature Control: No | Accessory: None
File: Internal Memory/17.01/5 RPM Spindle 6.vdt | Test Data Saved: 17/01/23 16:36 | Test Data Saved by: Administrator
Notes: None

Test Method

Test Method File Name: Unsaved Test | Test Method Saved On: | Test Method Created By:
Instructions:

Step (#)	Speed (RPM)	Temperature (°C)	Data Collection Type	Data Interval (hh:mm:ss)	Avg Duration (hh:mm:ss)	Collect point at step end	End Condition Type Oper. Val. Tol Unit	Density (g/cm³)	QC Limits Type Low High Unit
1	5.0	25.0	Single Point	OFF	OFF	OFF	Time = 00:00:30 OFF s	0.0000	None

Results

Test Averaging:

Step ()	Viscosity (cP)	Torque (%)	Speed (RPM)	Shear Stress (dyne/cm²)	Shear Rate (¹/s)	Temperature (°C)	Density (g/cm³)	Accuracy (+/-cP)
	0.00	0.0	0.00	---	---	---	0.0000	0.00

Step Averaging:

Step (#)	Viscosity (cP)	Torque (%)	Speed (RPM)	Shear Stress (dyne/cm²)	Shear Rate (¹/s)	Temperature (°C)	Density (g/cm³)	Accuracy (+/-cP)
1	60800	30.4	5.0	---	---	23.2	0.0000	2000

Gel Time (mm:ss)	Total Time (mm:ss)	Peak Temp (°C)	Peak Temp Time (mm:ss)
00:00:00.0	00:00:30.0	0.0,°C	00:00:00.0

DATA

Step (#)	Point (#)	Time (s)	Viscosity (cP)	Torque (%)	Speed (RPM)	Shear Stress (dyne/cm²)	Shear Rate (¹/s)	Temperature (°C)	Density (g/cm³)	Accuracy (+/-cP)
1	1	[illegible]	[illegible]	30.4	[illegible]	[illegible]	---	[illegible]	[illegible]	[illegible]

DVNXRVTJG 2.1.8.3-9 **VISCOSITY DATA REPORT** **17/01/23**

SAMPLE RUN INFORMATION

Test Start: 17/01/23 16:41 | Test End: 17/01/23 16:42 | Tester: Administrator
Instrument: RV (1.000000) | S/N: 86036486 | Model: DVNXRVTJG | FWV: 2.1.8.3-9
Spindle RV-07 (7) | S/N: 0 | SMC: 400.000 | SRC: 0.000 | YMC: 0.000
Global Limits: None | Temperature Offset: None | Temperature Control: No | Accessory: None
File: Internal Memory/17.01/50 RPM Spindle 7.vdt | Test Data Saved: 17/01/23 16:42 | Test Data Saved by: Administrator
Notes: None

Test Method

Test Method File Name: Unsaved Test | Test Method Saved On: | Test Method Created By:
Instructions:

Step (#)	Speed (RPM)	Temperature (°C)	Data Collection Type	Data Interval (hh:mm:ss)	Avg Duration (hh:mm:ss)	Collect point at step end	End Condition Type Oper. Val. Tol Unit	Density (g/cm³)	QC Limits Type Low High Unit
1	50.0	25.0	Single Point	OFF	OFF	OFF	Time = 00:00:30 OFF s	0.0000	None

Results

Test Averaging:

Step ()	Viscosity (cP)	Torque (%)	Speed (RPM)	Shear Stress (dyne/cm²)	Shear Rate (¹/s)	Temperature (°C)	Density (g/cm³)	Accuracy (+/-cP)
	0.00	0.0	0.00	---	---	---	0.0000	0.00

Step Averaging:

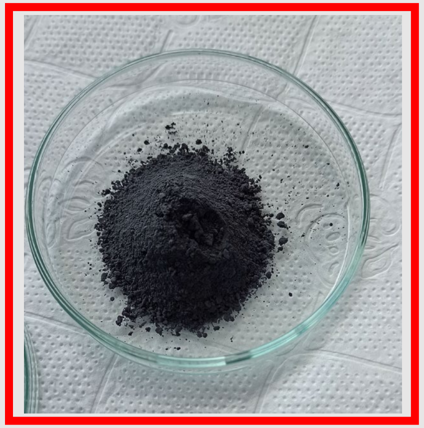
Step (#)	Viscosity (cP)	Torque (%)	Speed (RPM)	Shear Stress (dyne/cm²)	Shear Rate (¹/s)	Temperature (°C)	Density (g/cm³)	Accuracy (+/-cP)
1	49280	61.6	50.0	---	---	23.1	0.0000	800.0

Gel Time (mm:ss)	Total Time (mm:ss)	Peak Temp (°C)	Peak Temp Time (mm:ss)
00:00:00.0	00:00:30.0	0.0,°C	00:00:00.0

DATA

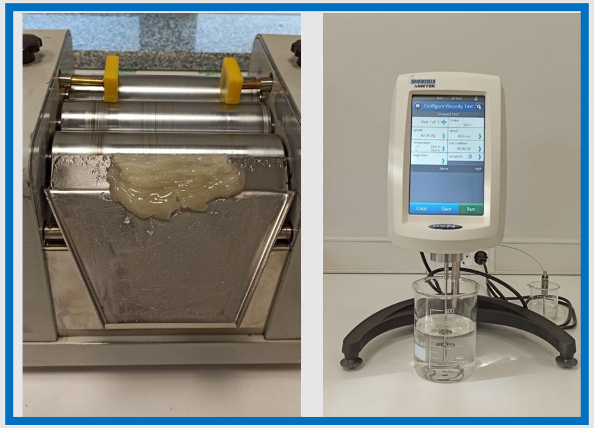
Step (#)	Point (#)	Time (s)	Viscosity (cP)	Torque (%)	Speed (RPM)	Shear Stress (dyne/cm²)	Shear Rate (¹/s)	Temperature (°C)	Density (g/cm³)	Accuracy (+/-cP)
1	1	30	49280	61.6	50.0	---	---	23.1	0.0000	800.0

Approach: Metal Paste

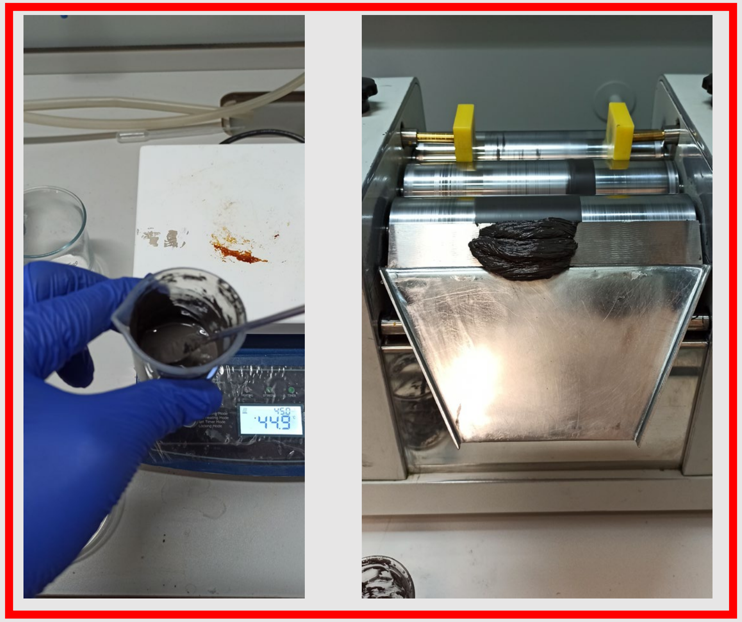


metal particles

glass frit



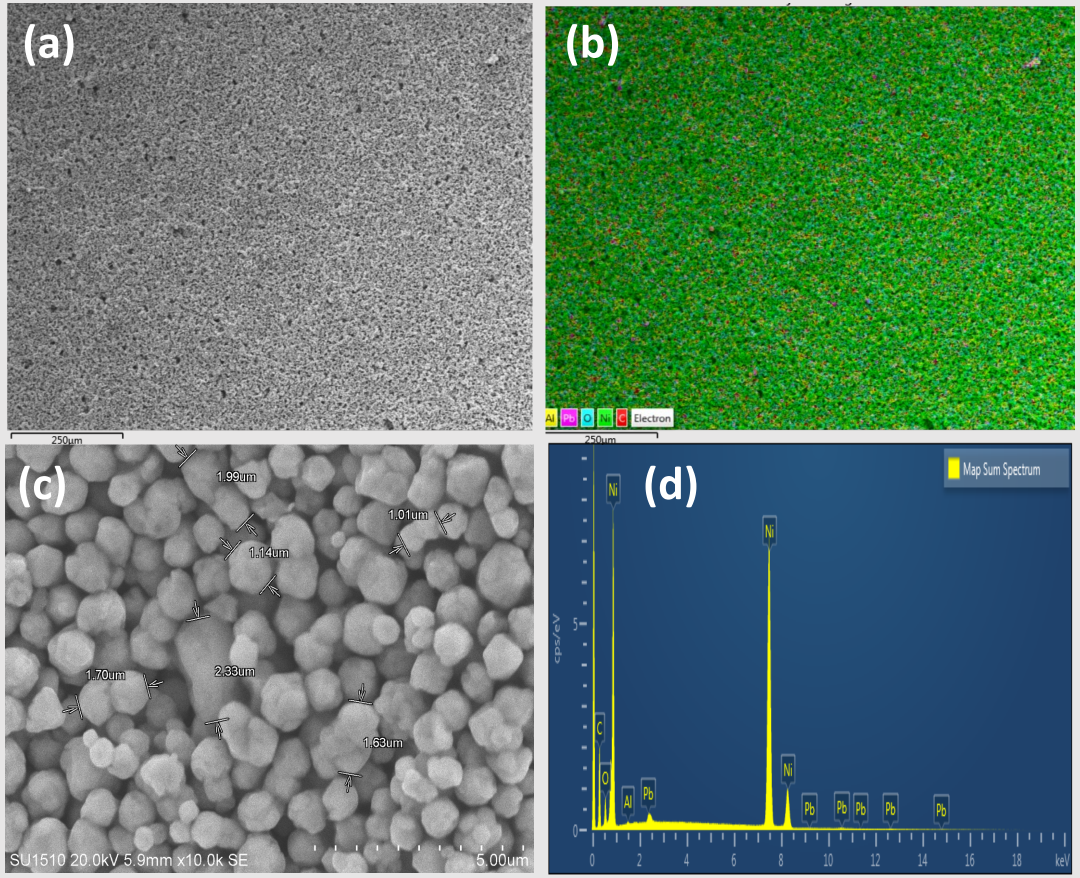
organic vehicle



Metal Paste

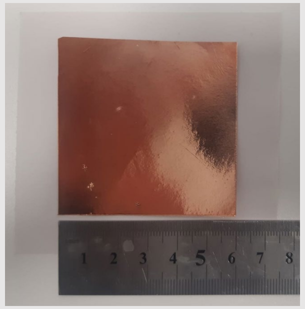
Approach: Metal Paste

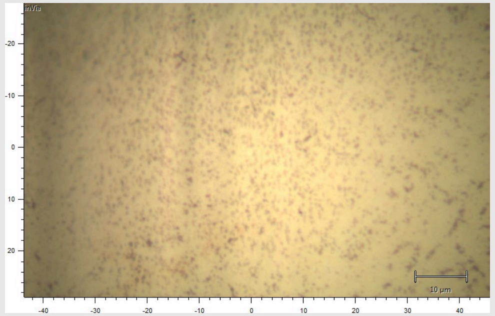
- All the prepared components:
  Metal Powder
  Glass Frit
  Organic Vehicle
  are then three roll milled



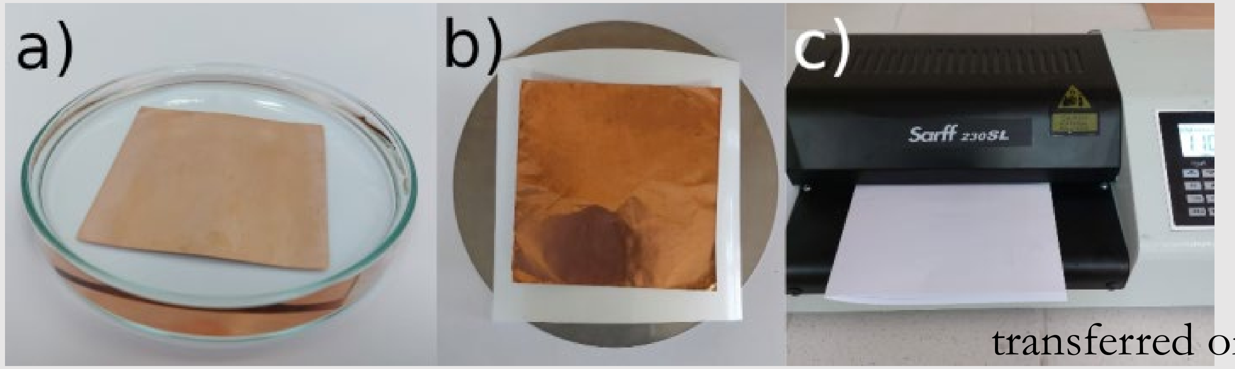
Approach: Graphene

- Graphene is grown on a copper foil
- Then it is transferred via a simple laminator on the wafer
- Optical images show somehow evenly distribution of graphene

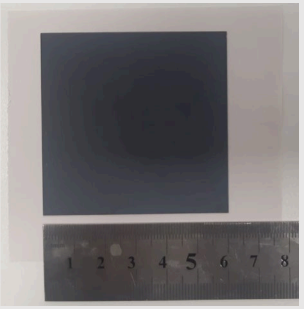


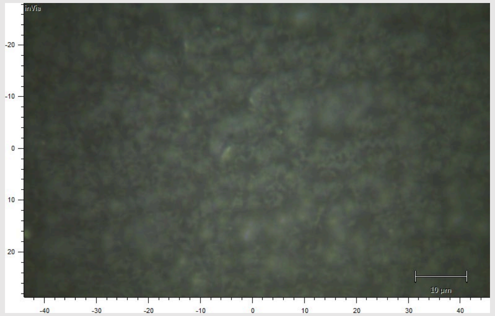


on a copper foil



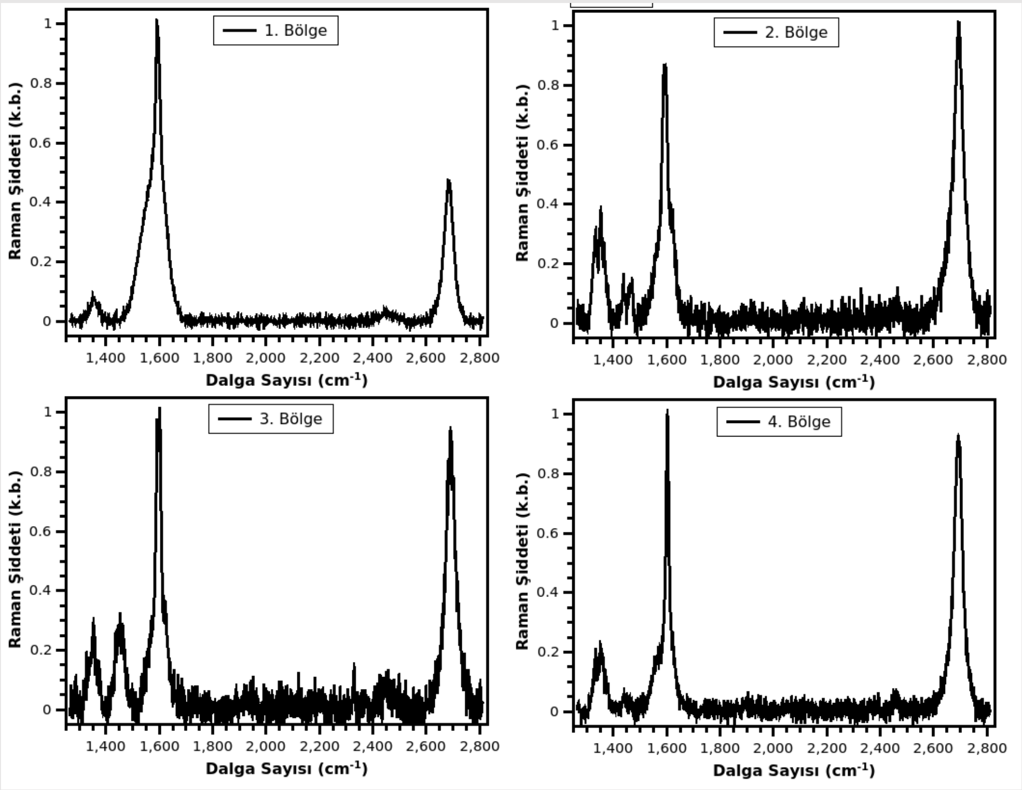
transferred onto acetate

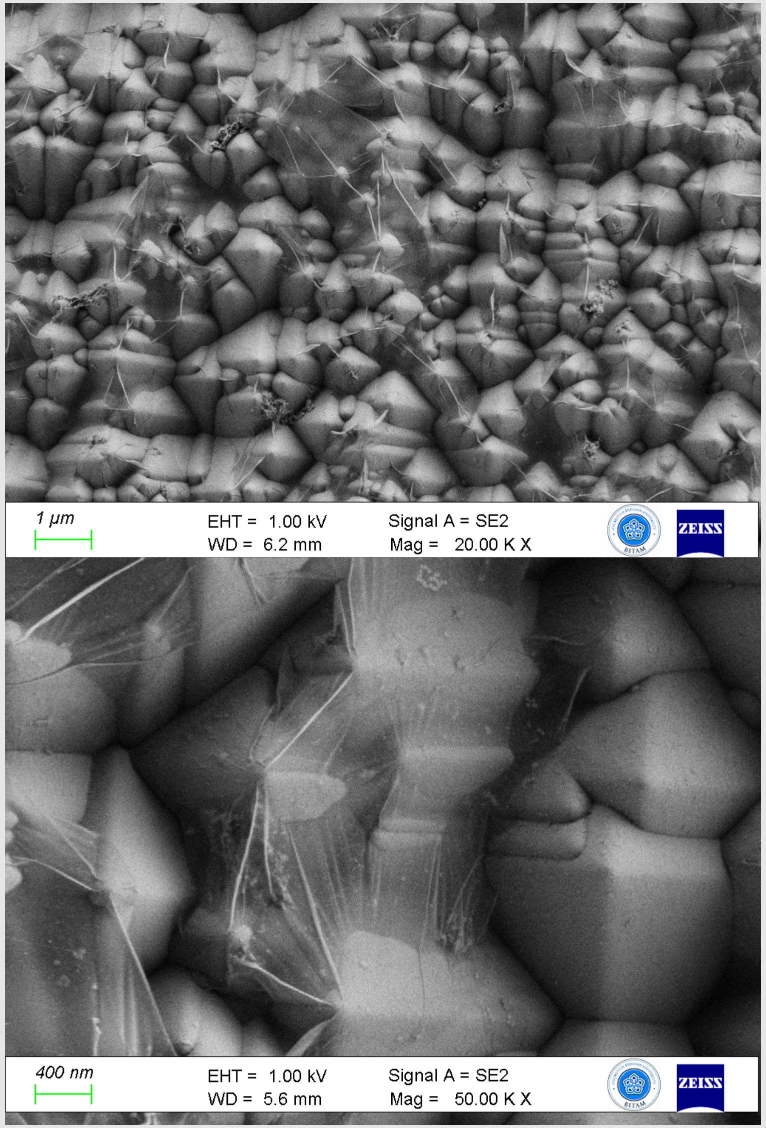




transferred onto the wafer

Approach: Graphene

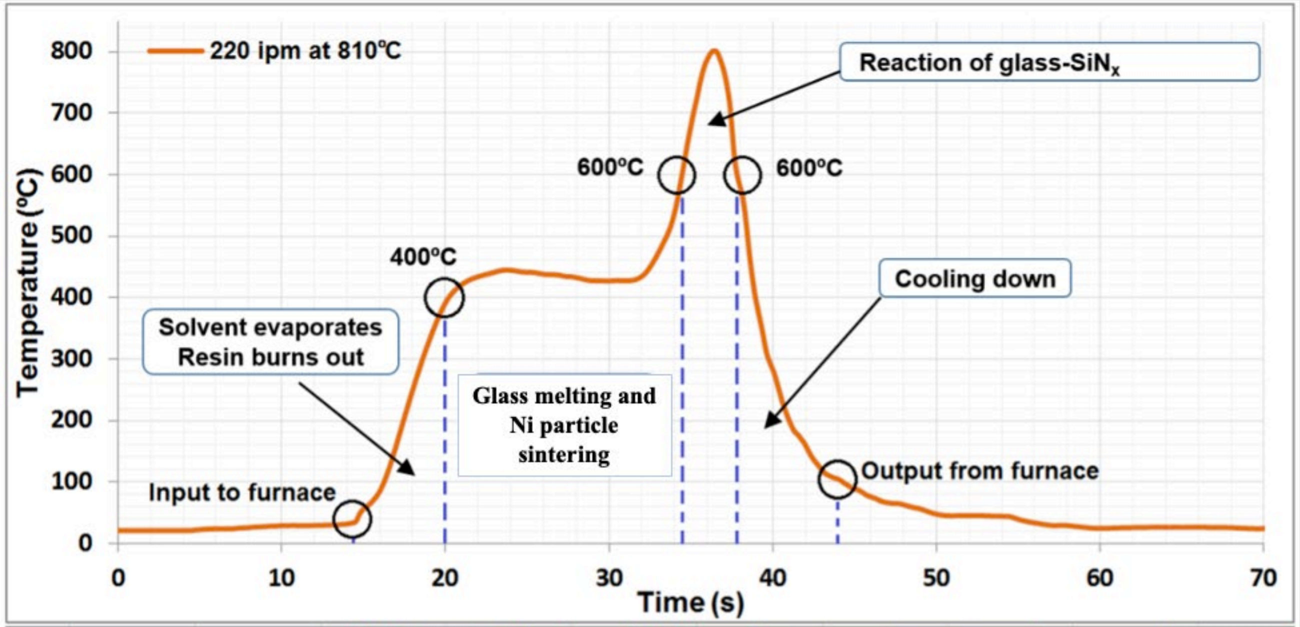




Approach: Screen Printing and Firing

- The metal pastes then printed onto the wafer with the graphene layer on top

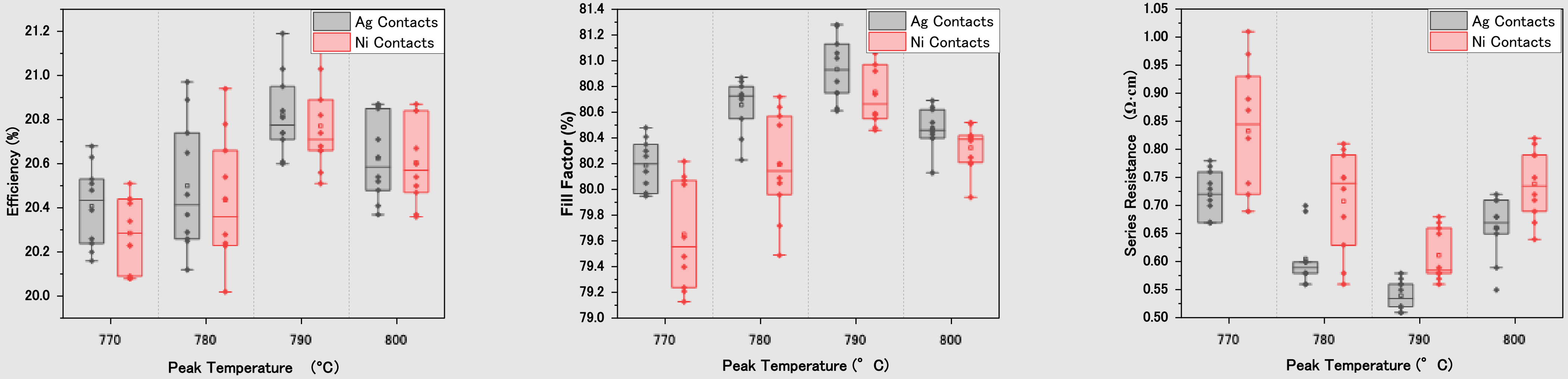
- The cell are finally fired with the similar temperature profile



		Maximum Temperature	Maximum Positive Slope	Maximum Negative Slope	Time Between Temperature	Time Above Temperature: Rising (+)	Time Above Temperature: Falling (+)	Time Above Temperature: Total (+/-)
					390-430°C	600°C	600°C	600°C
☑ Show All		°C	°C/sec	°C/sec	sec	sec	sec	sec
☑ A2	Sensor 2 Location	801.7	127.83	-190.04	1.6	1.9	1.4	3.4
	Range	0.0	0.00	0.00	0.0	0.0	0.0	0.0
	Average	801.70	127.830	-190.040	1.60	1.90	1.40	3.40
	Std Deviation	-1.#IO	-1.#IND	-1.#IND	-1.#IO	-1.#IO	-1.#IO	-1.#IO
		Template: C:\ECD\MegamoleMAP\Template\DataTableCalculations.tpf						

Results

Electrical Measurement

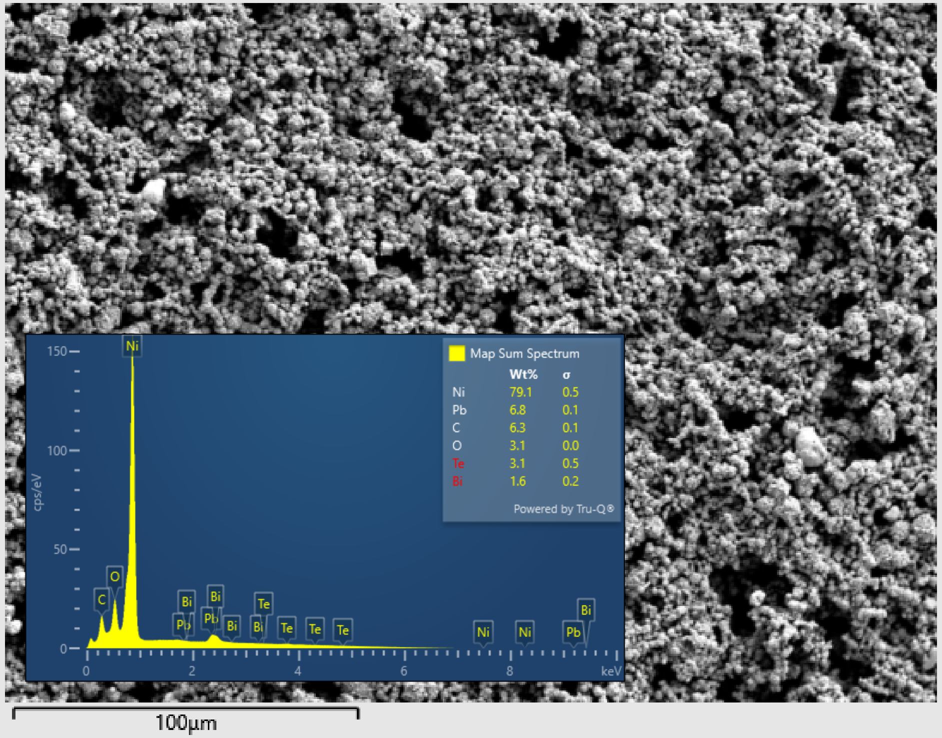


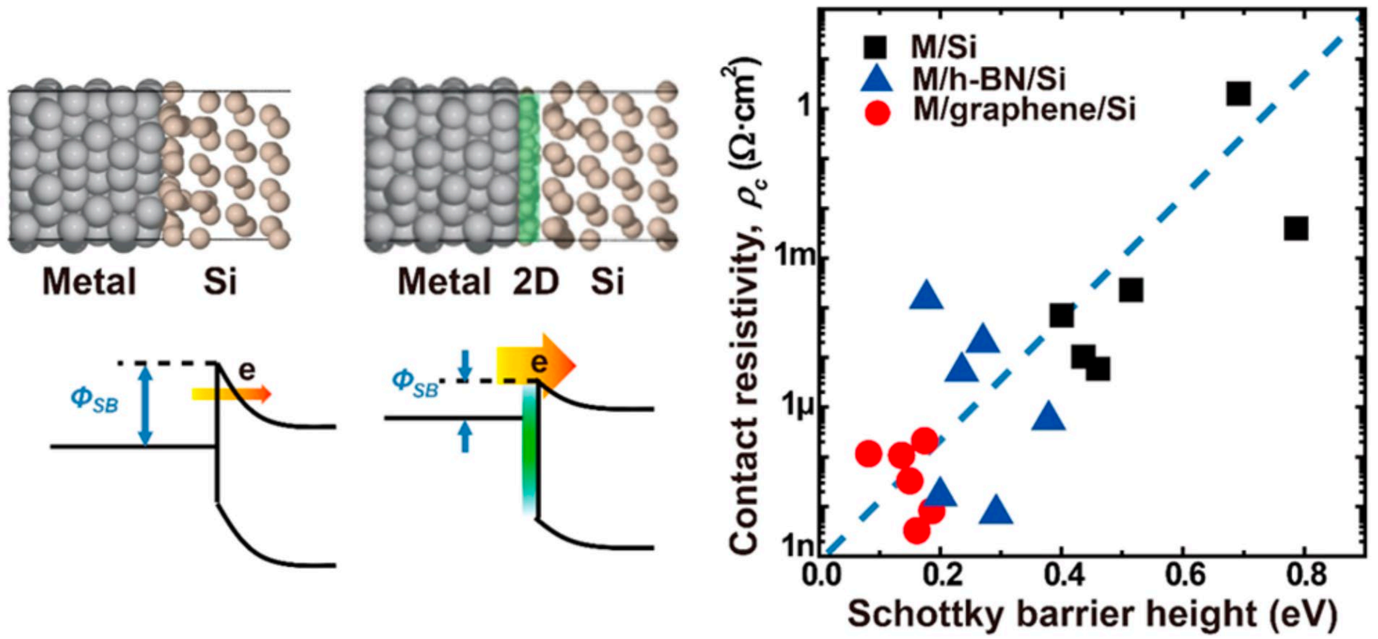
- The mean lateral finger resistance for the Ni contacts is 1.1Ω/cm while the Ag contacts yielded 1Ω/cm.
- The mean contact resistance for the Ni contacts is 5.2 mΩ·cm^2 while the Ag counterpart is 4.8 mΩ·cm^2

Results

Microstructure analysis

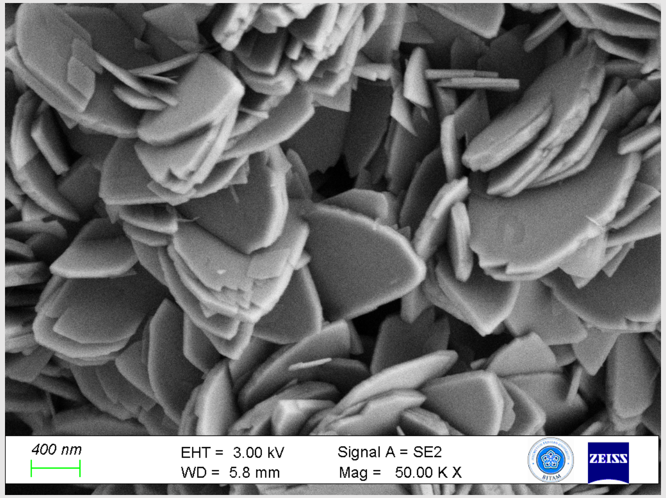
Electron Image 4



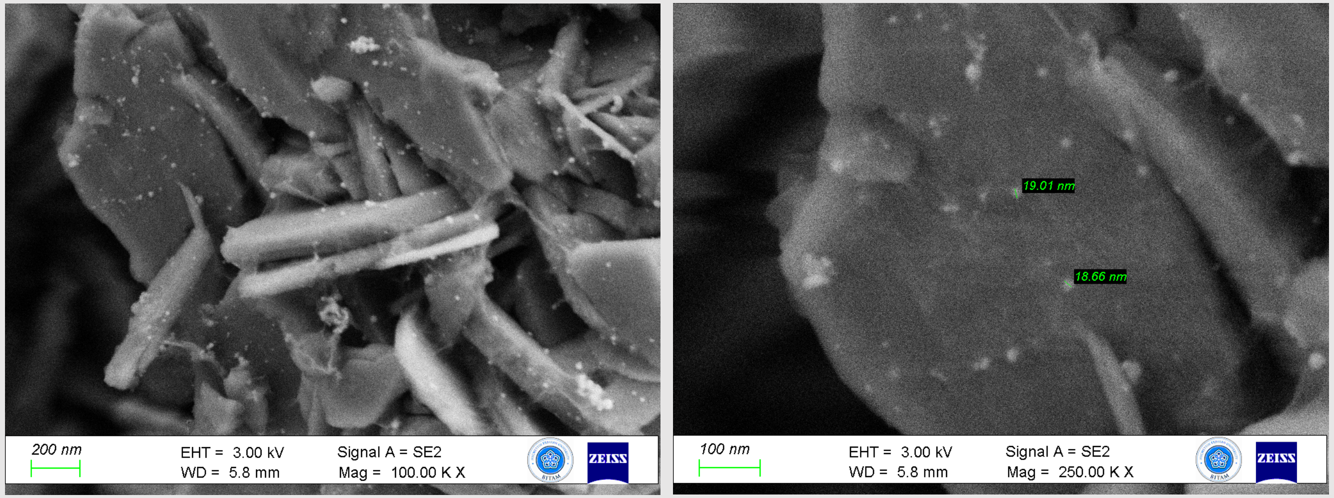


Future Work and Conclusion

- This study is a proof of work on screen printable Ni contacts.
- The challenge is to have the graphene layer transferred onto the Si before metallization.
- To avoid this, doping the graphene onto Ni powder creates the same effect on the metal work function



Surface treated Ni



Surface treated Ni with doped powder

Metallization & Interconnection WORKSHOP

Thank you for your attention!

Questions?

Veysel Unsur, Ph.D.[1,2]

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