Zinc Oxide Based Inks for Semi conductive Applications

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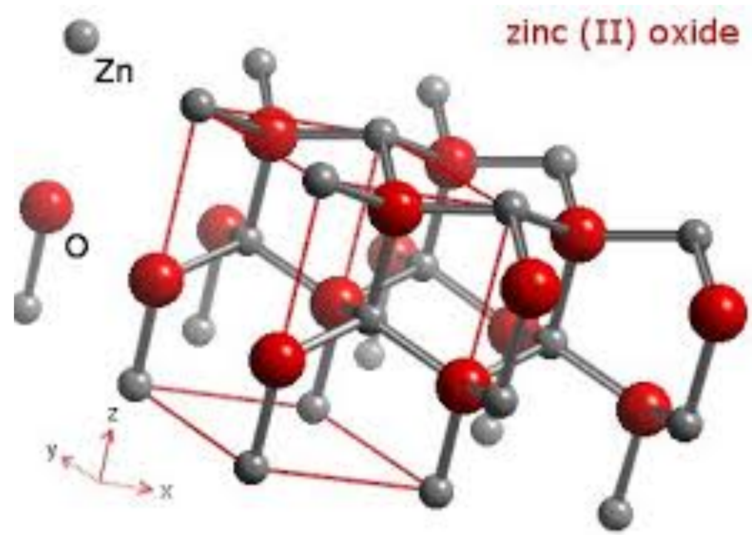
Agenda

- n- and p- type semiconductive ZnO
- Application in Printed Electronics
- Experimental-Formulating semiconductive ZnO inks
- Results- Printing,Sintering, and Testing ZnO inks
- Conclusion

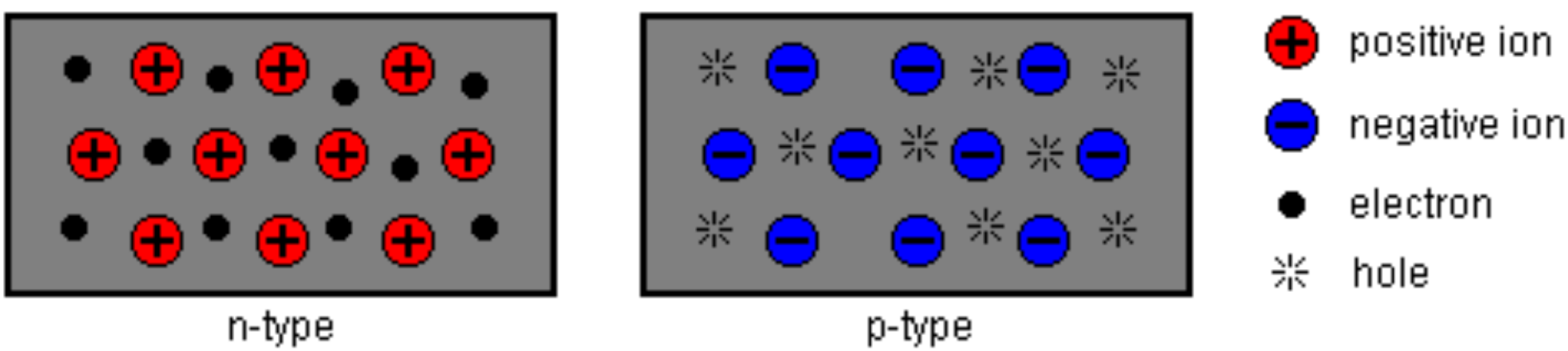


Doped ZnO - Semiconductor

- n-type (Higher electron mobility)
- p-type (Higher hole mobility)

Adding impurities to certain semiconductors:

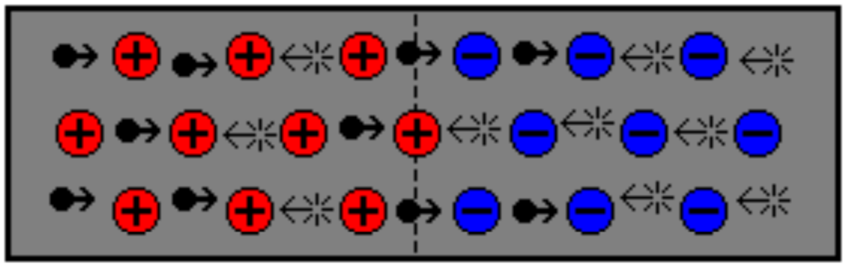
n-type converted to p-type and back



http://www.madlab.org/electrnx

ZnO Applications

- Transparent conductive coatings
- Electrodes for dye- sensitized solar cells
- Field emission materials
- Transistors
- Gas sensors
- Temperature sensors
- Light Emitting Diodes



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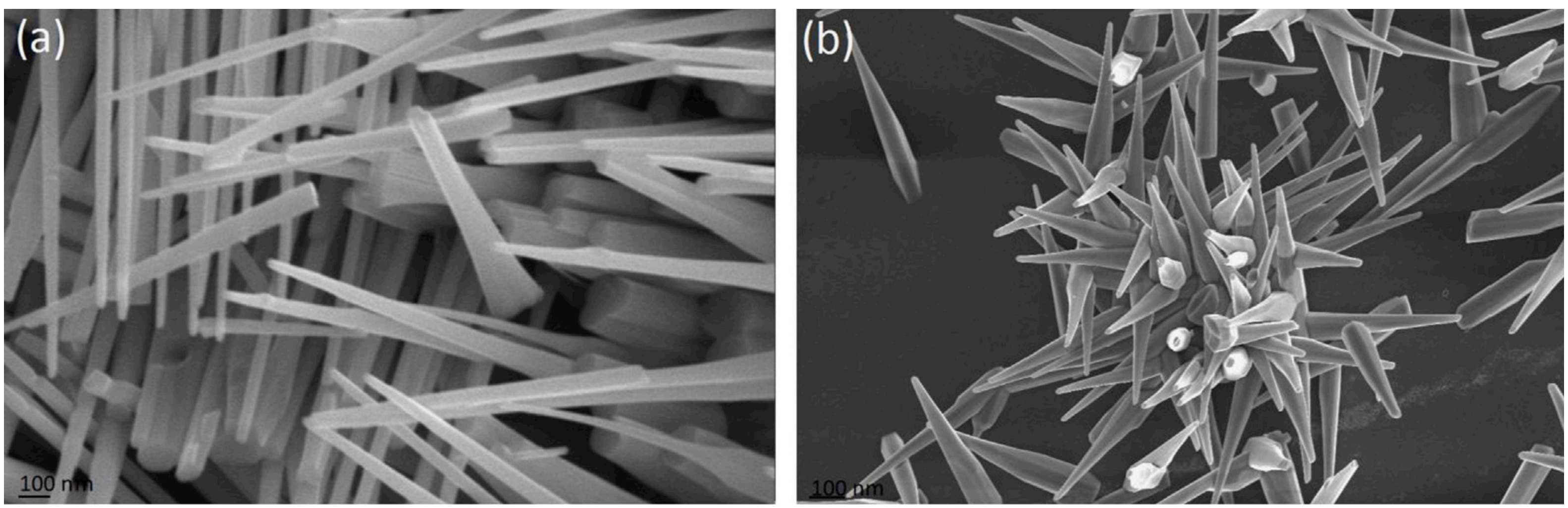
The Aim of This Work

- **To formulate** semi conductive **ZnO ink** for rotogravure printing to be cured by photonic sintering.
- To enhance semi conductive behavior by doping with different metals.
  - Various concentrations of **Ag** silver and **Al** aluminum were applied as **dopants** to achieve **semi conductive** behavior.

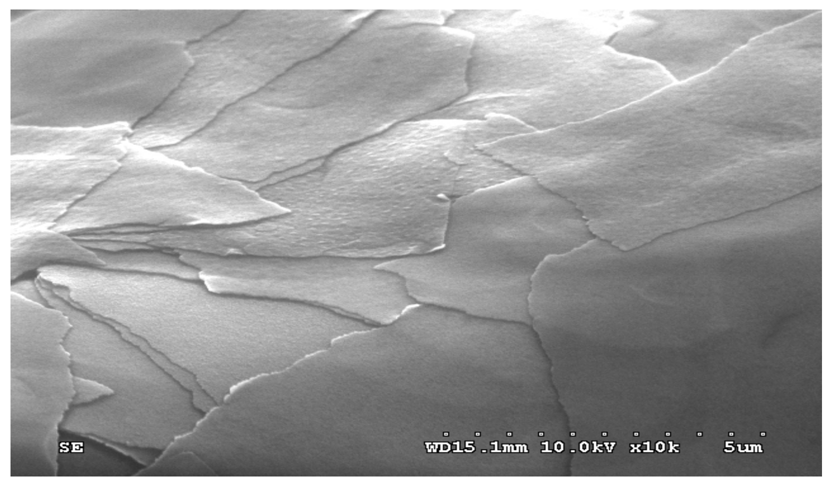
Experimental



ZnO Ink Formulations

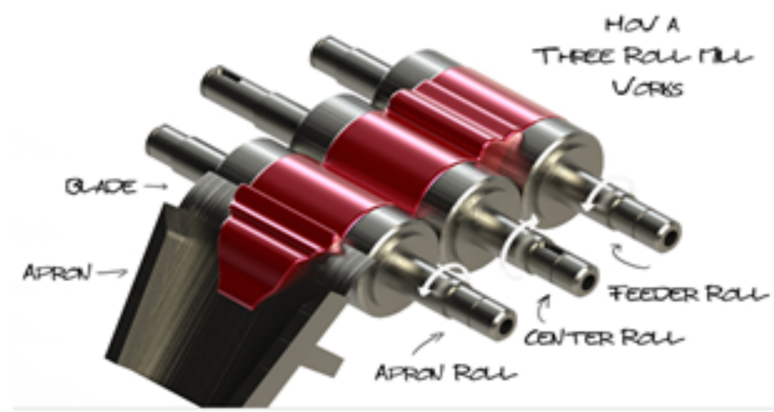
- Various forms of ZnO
- Solvent based acrylic resins
- **Silver dopant** - silver ink from InkTec® PR-020
- **Aluminum dopant**-Vacuum metalized flake aluminum pigment –VMP from Silberline

Aluminum Solvent Based Ink



Zinc Oxide

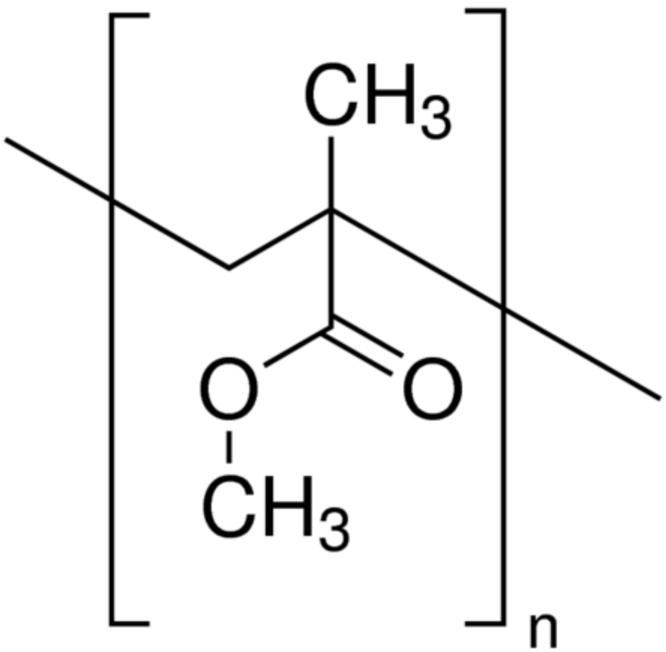
- Commercial zinc oxide from Alfa Aesar®
- Particle size 74 microns
- Dispersed in isopropyl alcohol (IPA)
- Milled-2 passes on three roll mill
- Final particle size 1 micron
-



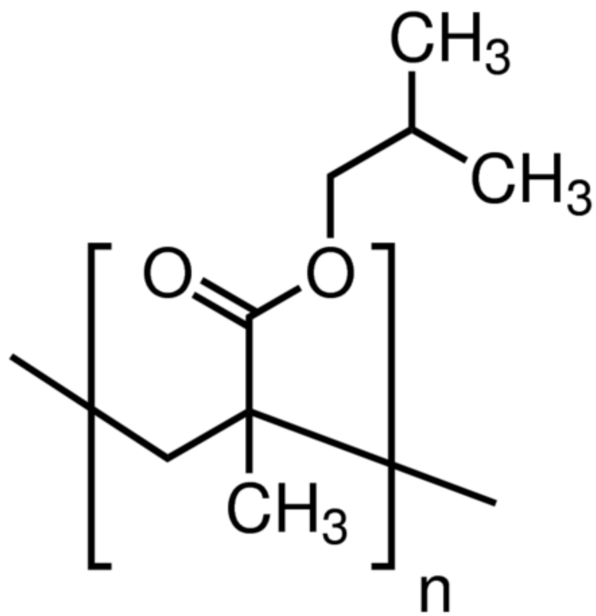
Elvacite Resins

- Elvacite® 1010 and Elvacite® 2045 by Lucite International
- Elvacite 1010 - a low molecular weight methyl methacrylate polymer
- The key feature of this resin is that it maintains a fairly low viscosity.
- Elvacite 2045 is a high molecular weight iso-butyl methacrylate resin, has superior binding strength and good burn out characteristics as outlined by the manufacturer.

Methyl Methacrylate (L) and Iso-Butyl Methacrylate (R)



Elvacite® 1010
MW 4000 - 10,000



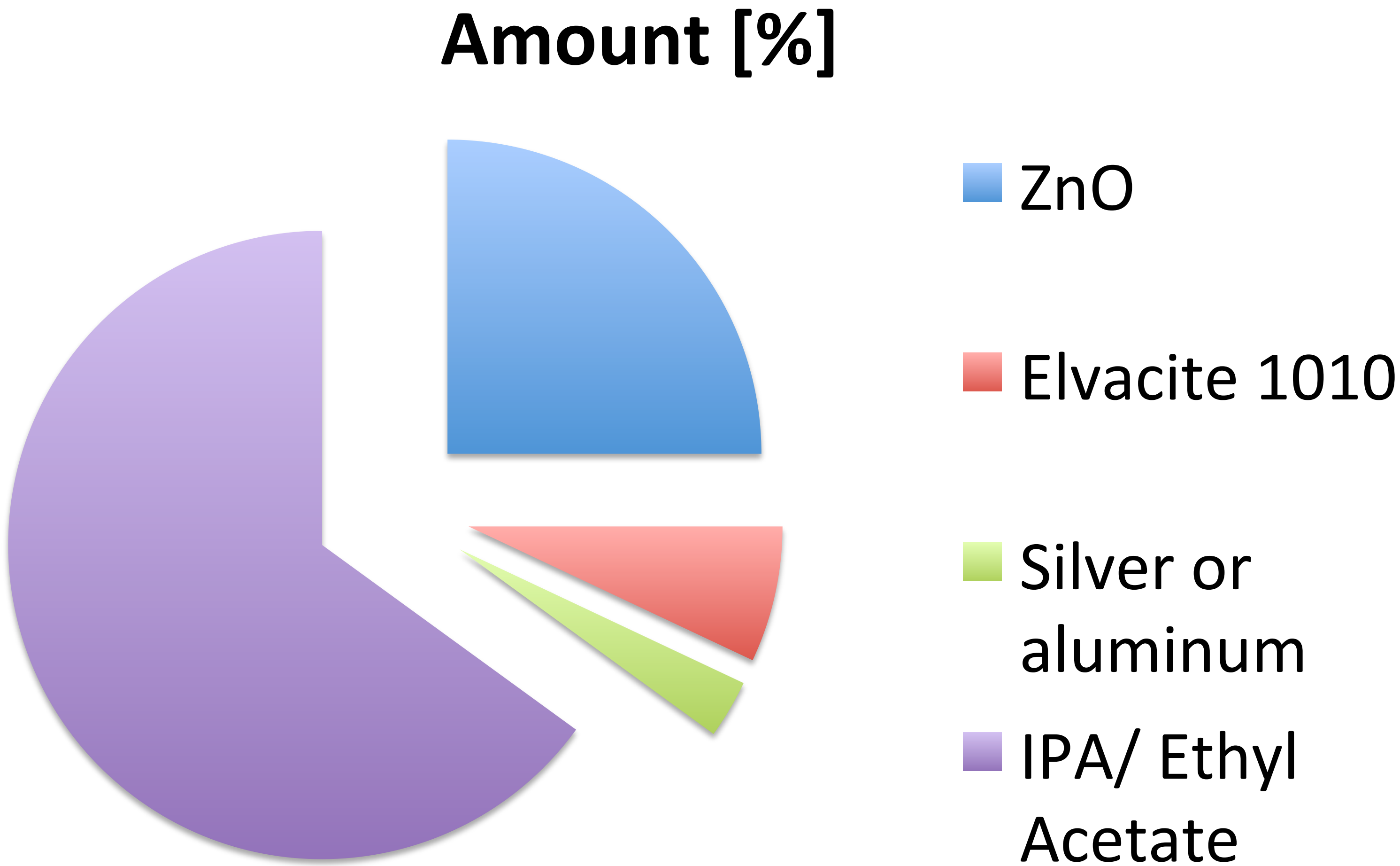
Elvacite® 2045
MW 193,000

Ink Formulations with Elvacite® 1010

Target Solids (%) 25 – 43

Components	Name	Amount (%)	Dry Weight (g)
Filler	ZnO	20 – 30	32.5 – 48.7
Binder	Elvacite 1010	4 - 8	8.1 – 16.2
Dopant	Silver or aluminum	1 – 5	1.6 – 8.1
Solvent	IPA: Ethyl Acetate	75 -57	

ZnO Ink Formulation

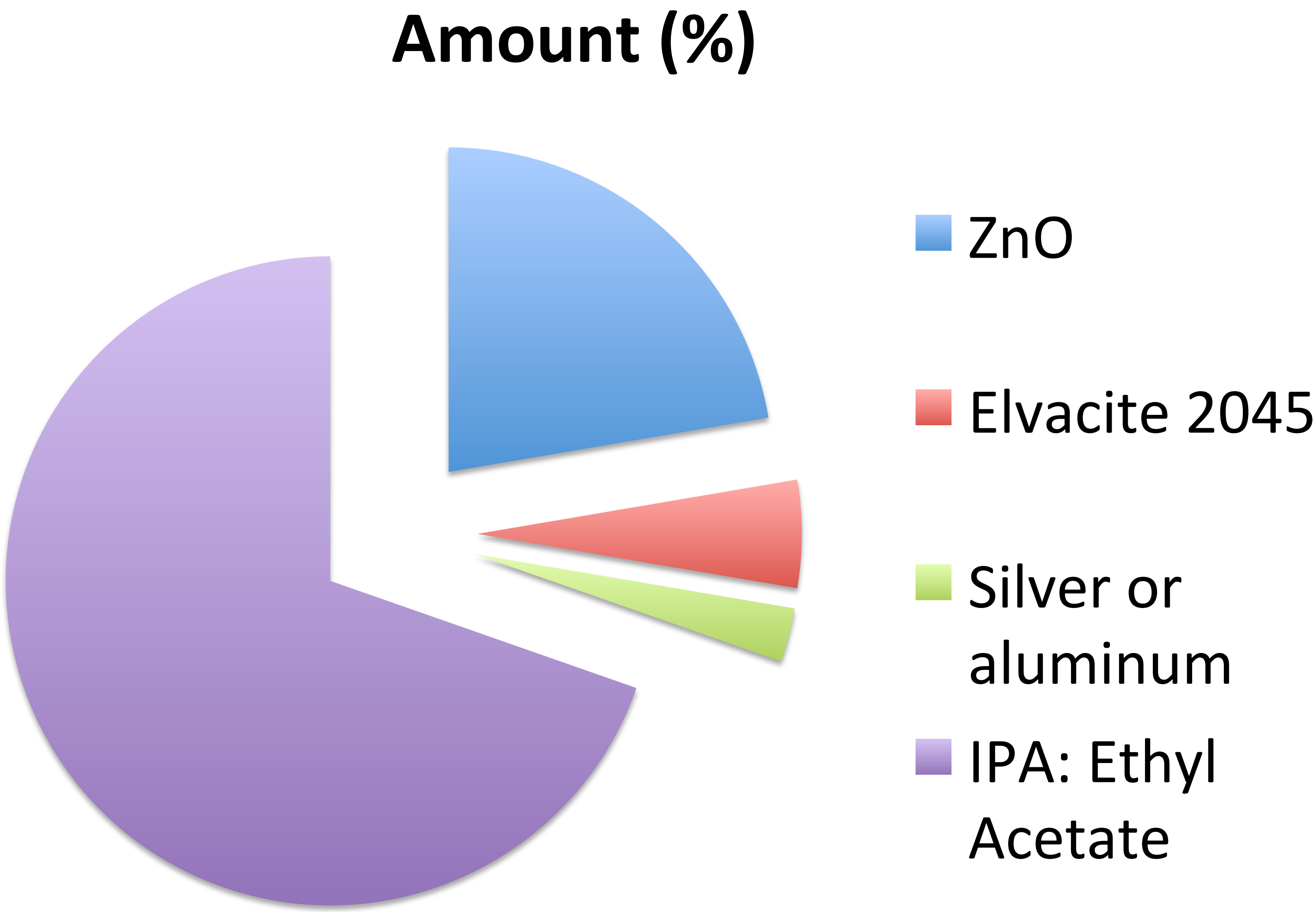


Ink Formulations with Elvacite® 2045

Target Solids: 26 %– 44 %

Components	Name	Amount (%)	Dry Weight (g)
Filler	ZnO	21 – 30	32.5 – 46.4
Binder	Elvacite 2045	4 - 8	6.5 – 13
Dopant	Silver or aluminum	1 – 6	1.6 – 9.7
Solvent	IPA: Isopropyl Acetate	74 - 56	

ZnO Ink with Elvacite 2045

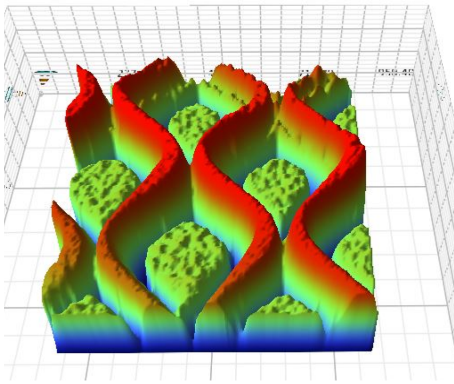


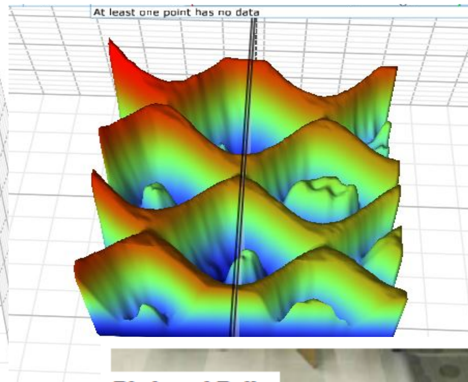
Ink Formulations Combining Elvacite® 1010 and Elvacite® 2045

Target Solids 33 – 39 %

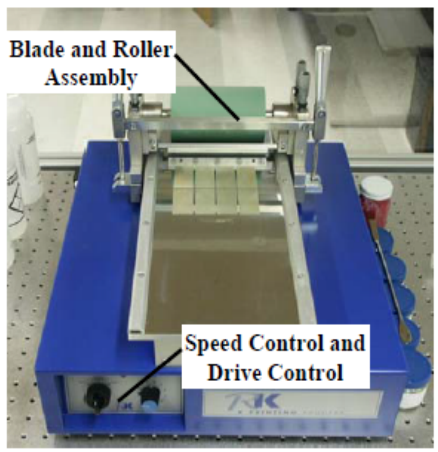
Components	Name	Amount (%)	Dry Weight (g)
Filler	ZnO	25	32.5 - 46.4
Binder	Elvacite 1010 Elvacite 2045	4 2-4	8.1 3.2-6.5
Dopant	Nano Silver	2 – 6	1.6-9.7
Solvent	IPA: Ethyl Acetate-Iso Propyl Acetate	67.9 – 61	

Gravure K-Proofer Printing

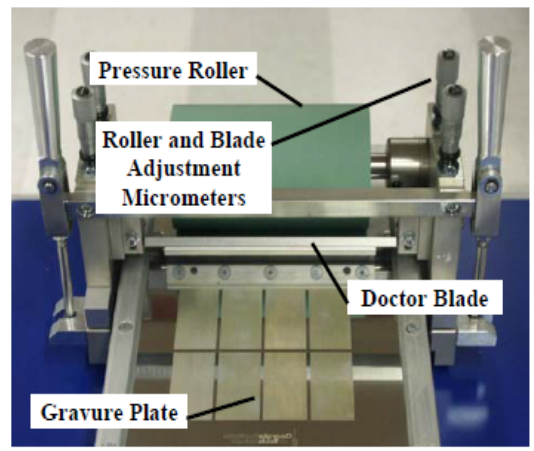




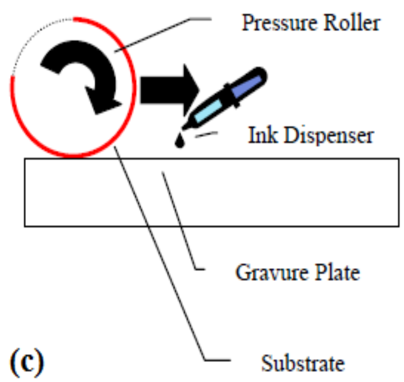
100 LPI AND 160 LPI ENGRAVED K-PROOFER PLATE



(a)



(b)

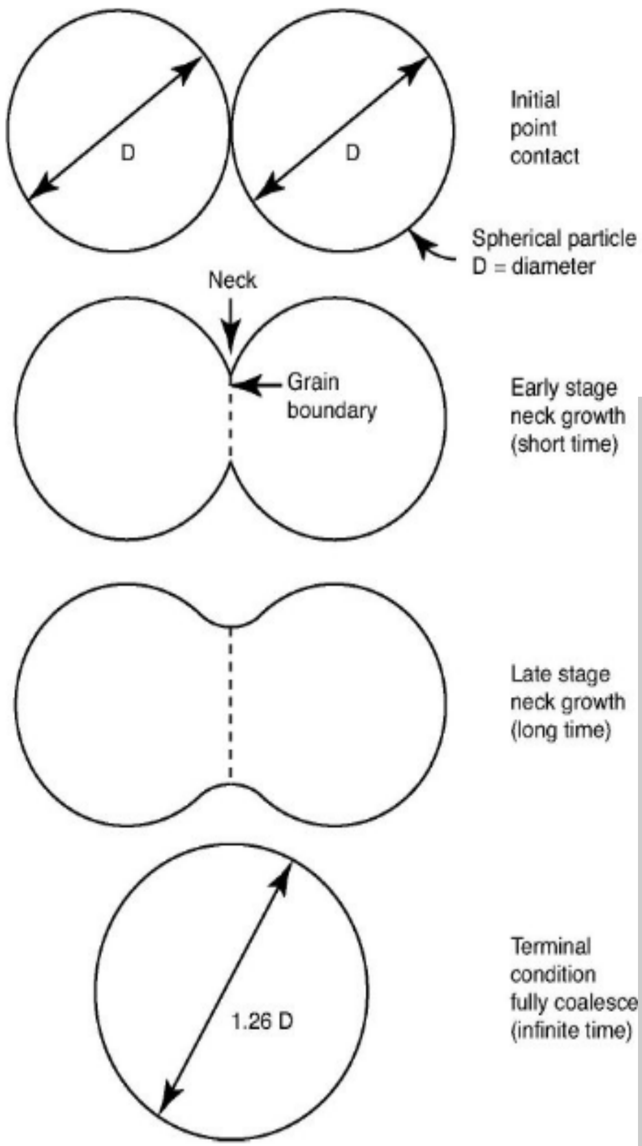


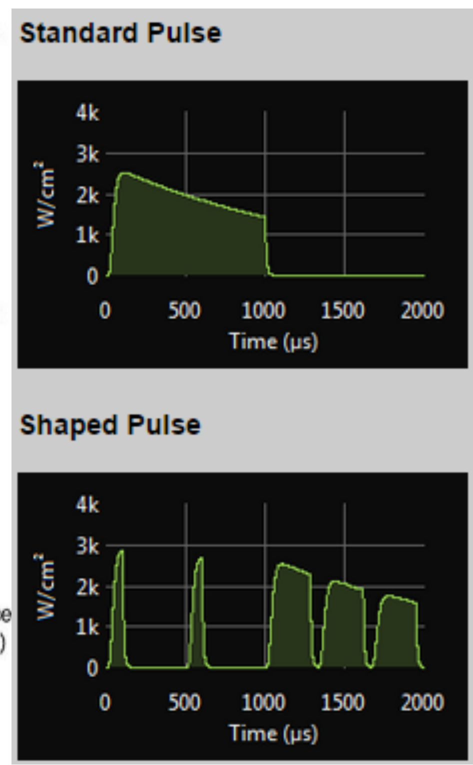
(c)

Sintering Parameters for PulseForge® 1200

Parameters	Levels
Diode Voltage (V)	300 – 430
Pulse Length (µs)	600 – 1000
Web Speed (feet/min)	10 fpm – 20 fpm
Web Height	25 mm
Energy (W/cm^2)	3.5 k – 5.2 k
Sim Pulse® Temperature (°C)	1070° C

PulseForge® 1200 Photonic Curing

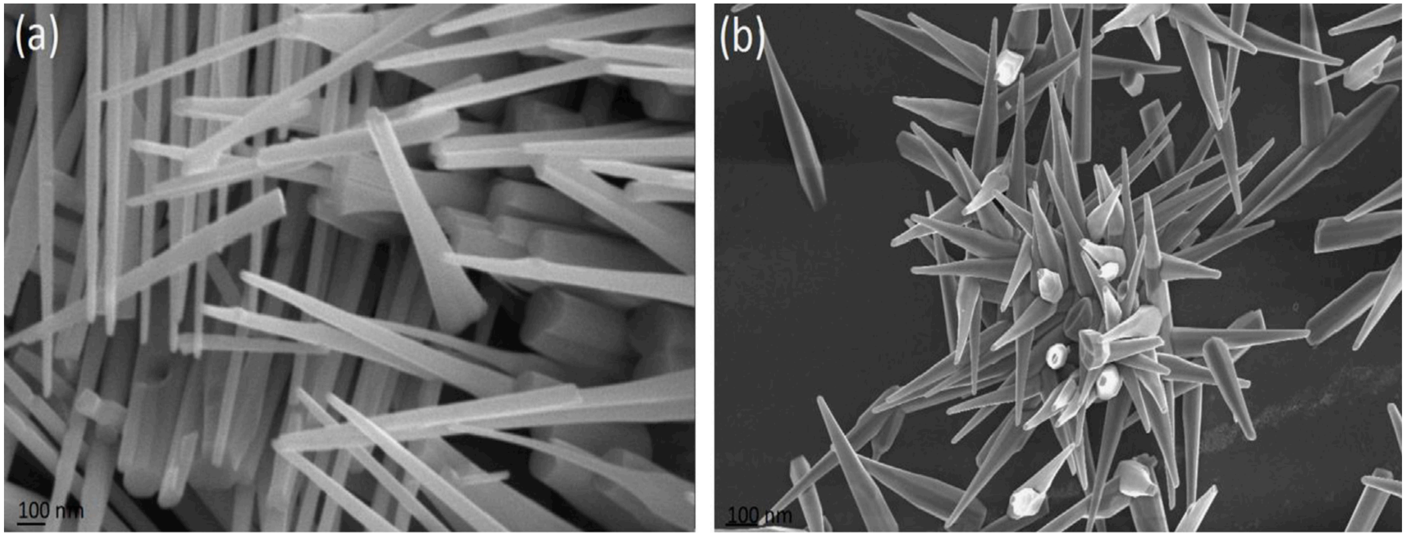




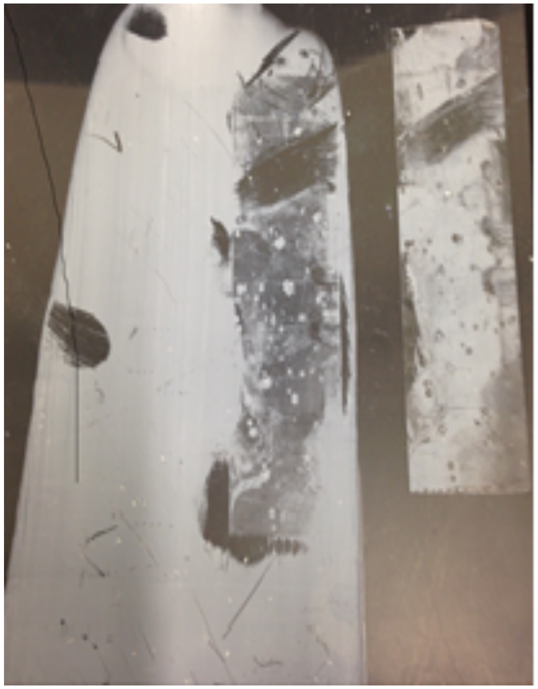
Design of Experiments (DOE) with Three Factors at 2 Levels

Run no.	ZnO (%)	Resin (%)	Doping (%)
1	30	7	2
2	30	7	4
3	22	7	4
4	22	4	4
5	30	4	2
6	30	4	4
7	22	7	2
8	22	4	2

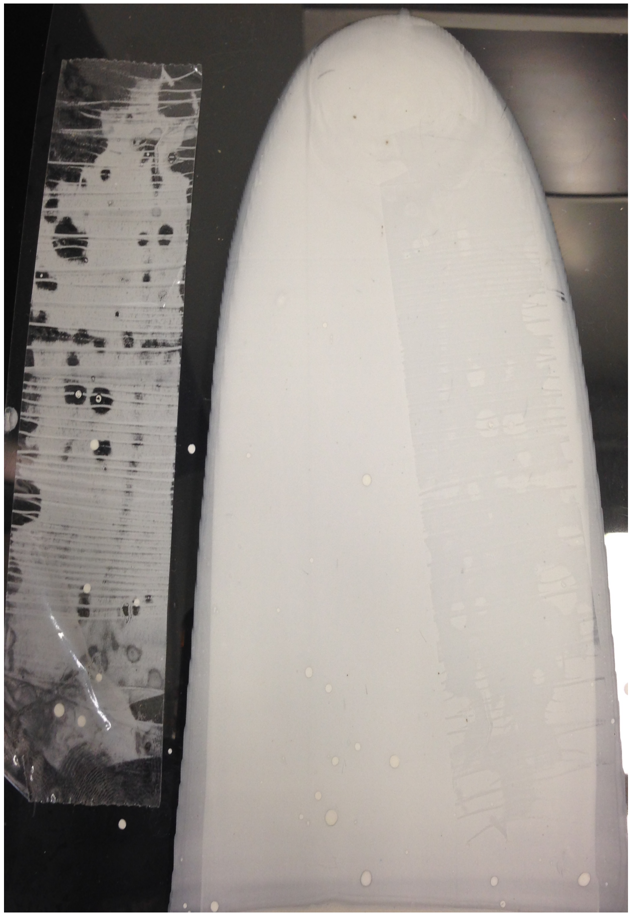
Results



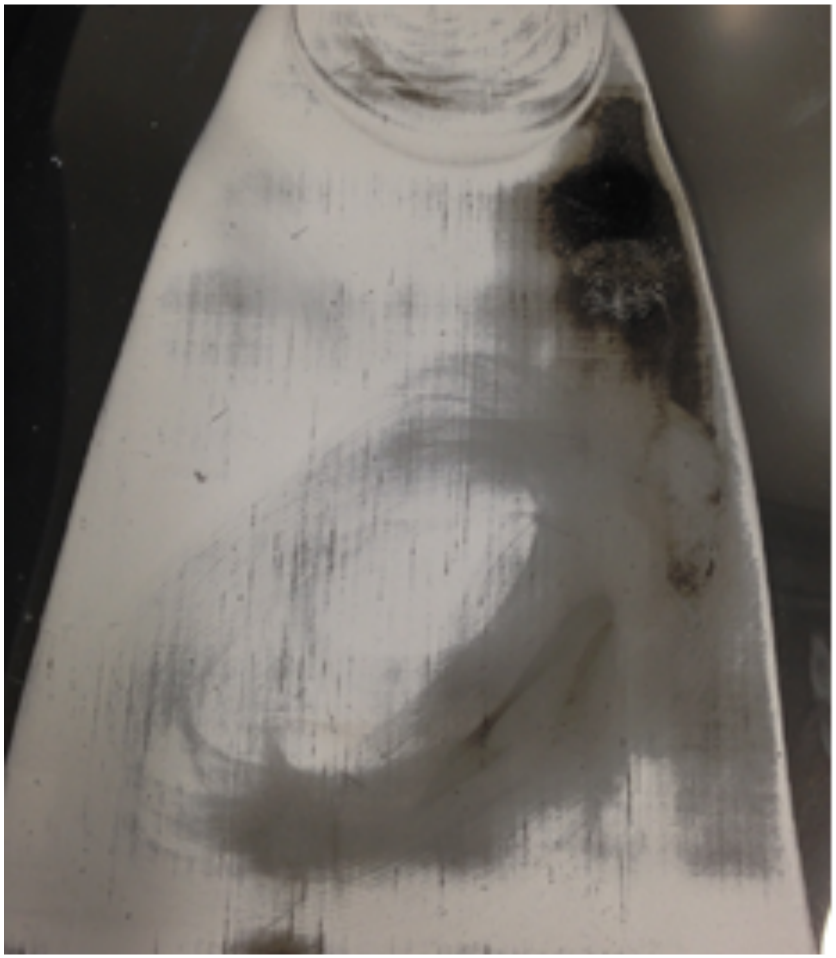
Difference in 4% (L) and 8% (R) resin Elvacite® 1010 for ZnO adhesion

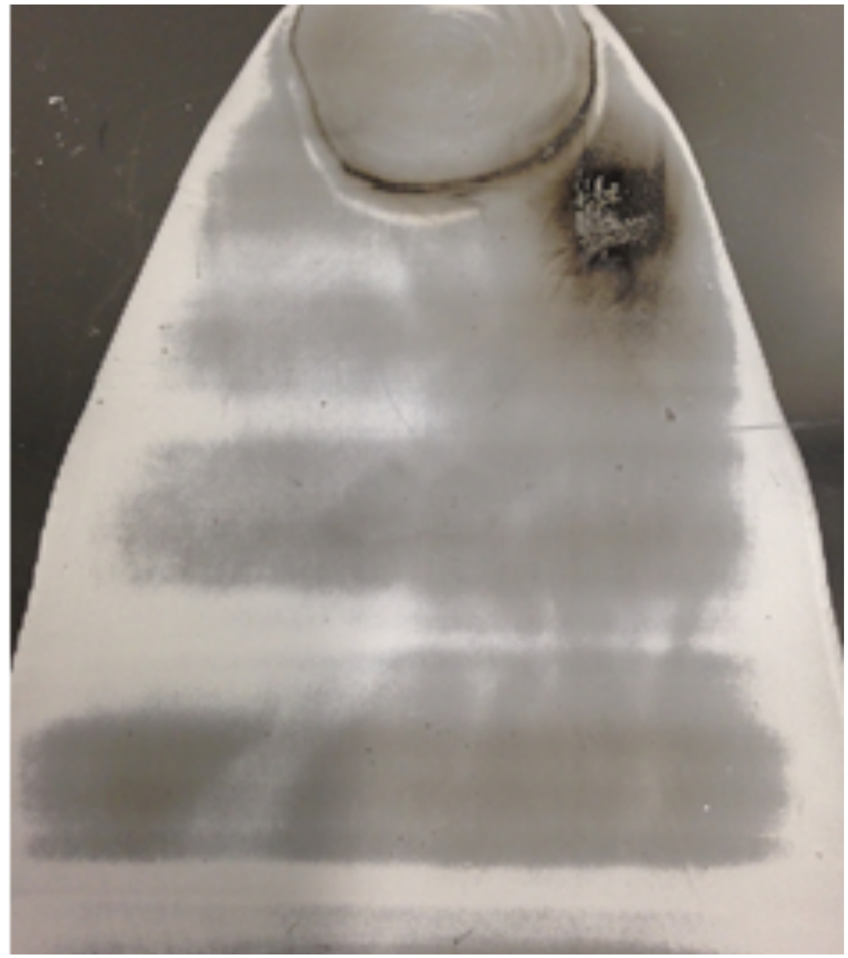


Adhesion test for Elvacite® 2045



Burn off when doped with Aluminum

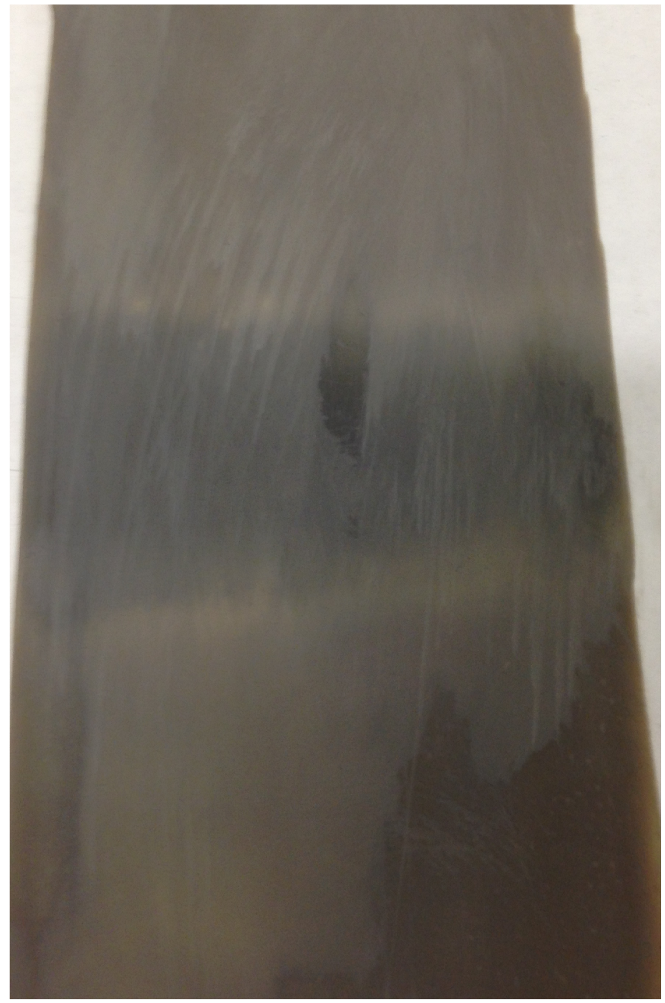




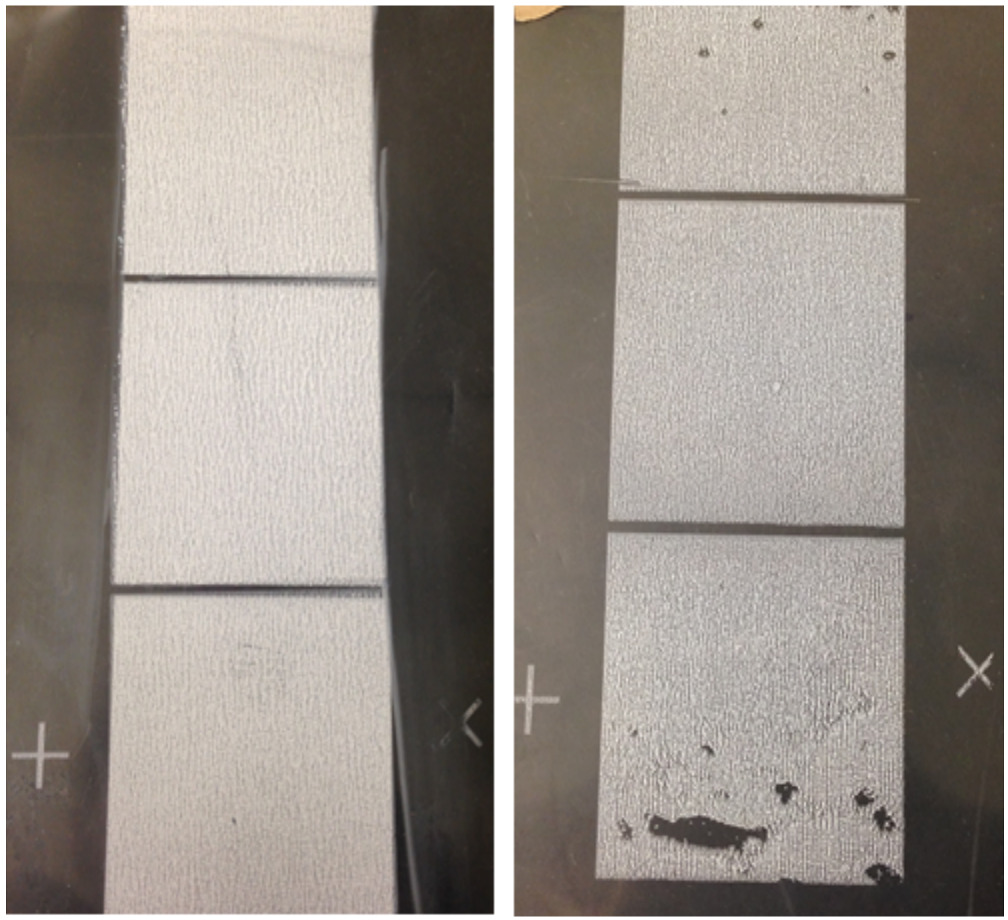
Nano ZnO w/Silver- Sintered

Original Settings

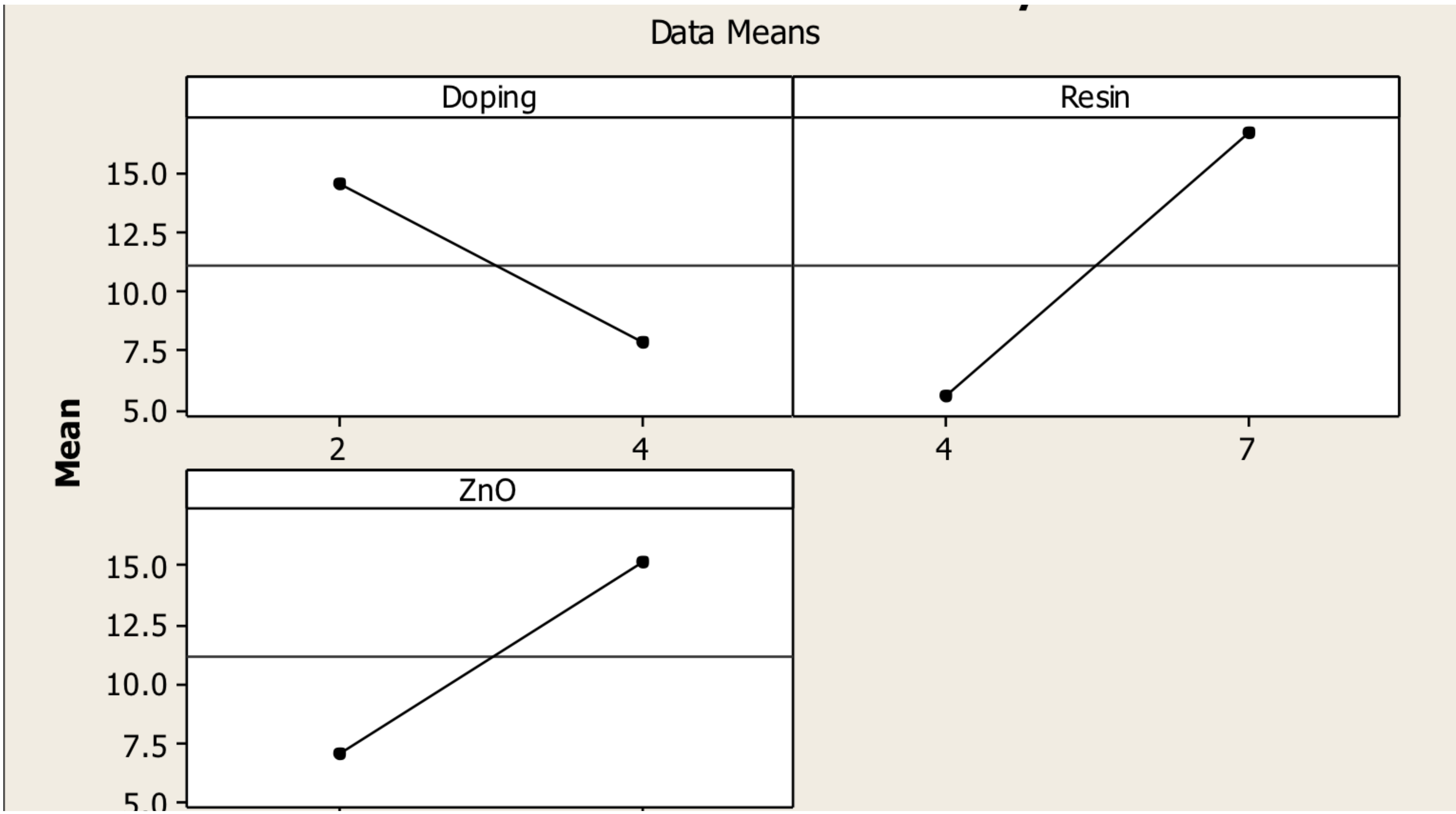
Reduced Diode Voltage



100 LPI (L) and 160 LPI (R) Prints on Gravure K-proofer



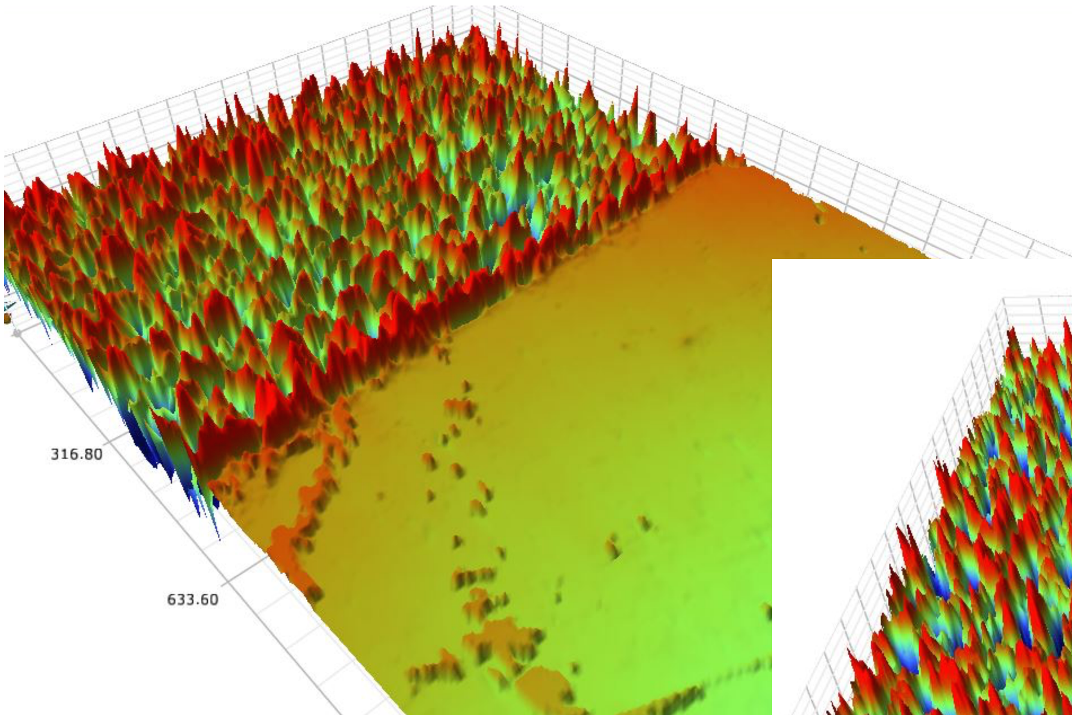
Design of Experiment Results



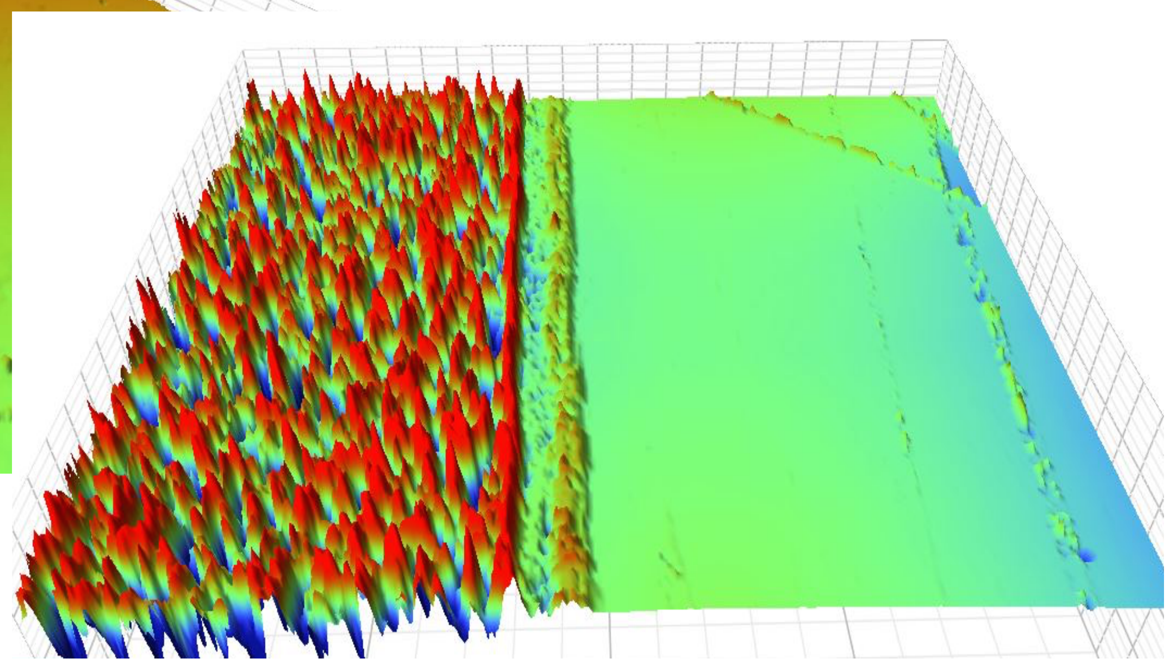
Best Ink

Run no.	ZnO (%)	Resin (%)	Doping (%)
1	30	7	2
2	30	7	4
3	22	7	4
4	22	4	4
5	30	4	2
6	30	4	4
7	22	7	2
8	22	4	2

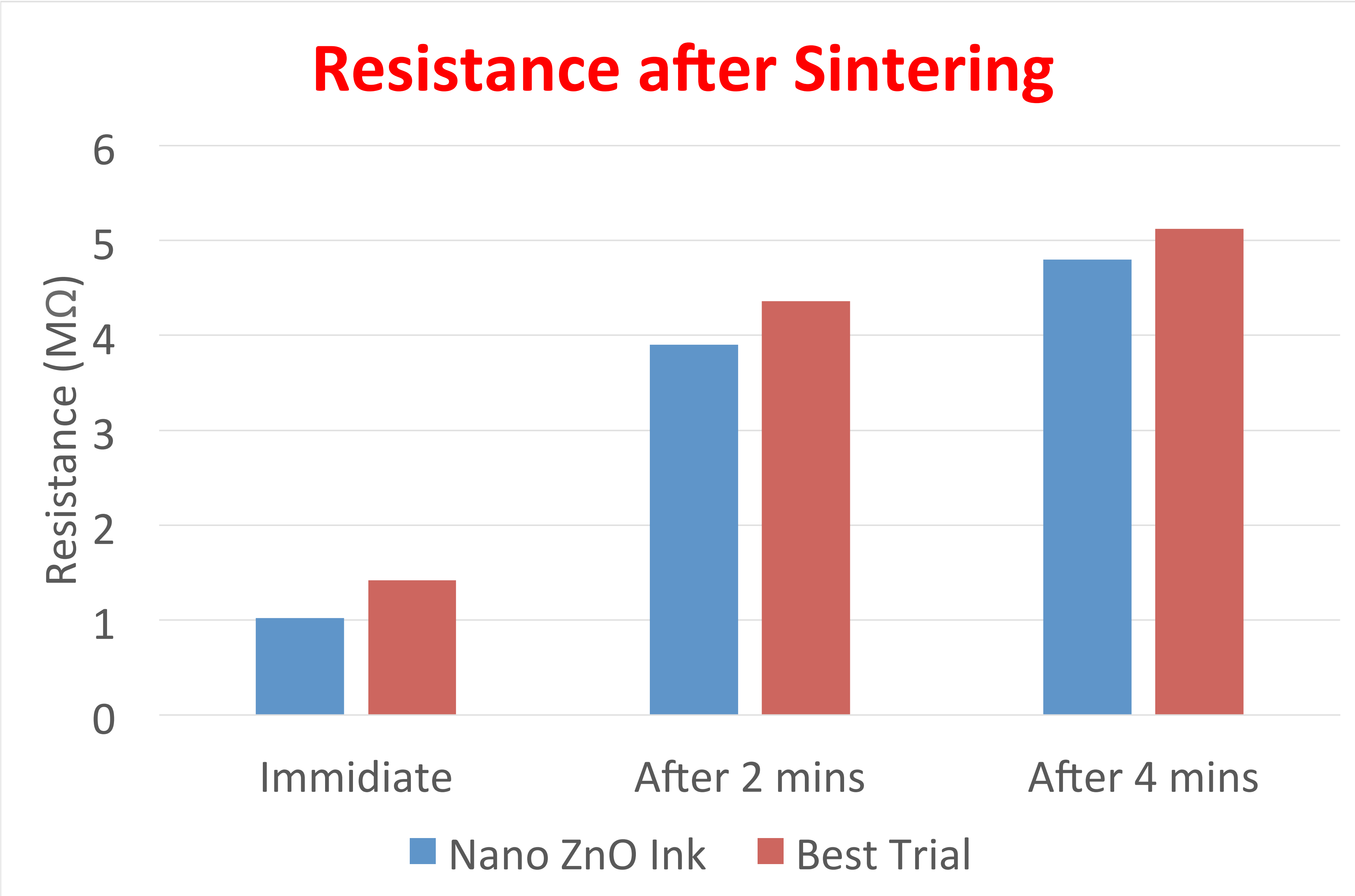
AFM image of ZnO/Ag Sintered Inks



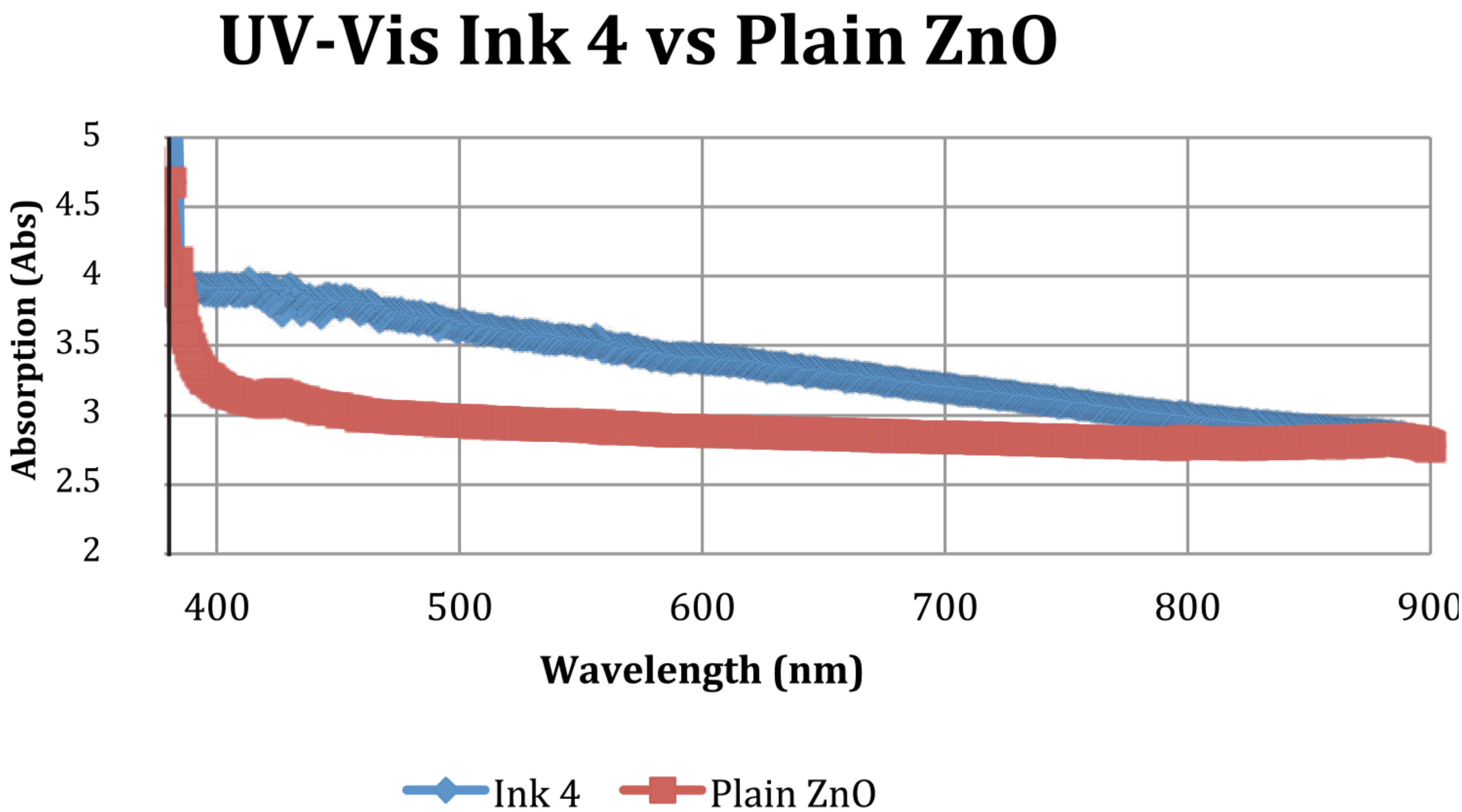
ZnO Nanoparticle ink



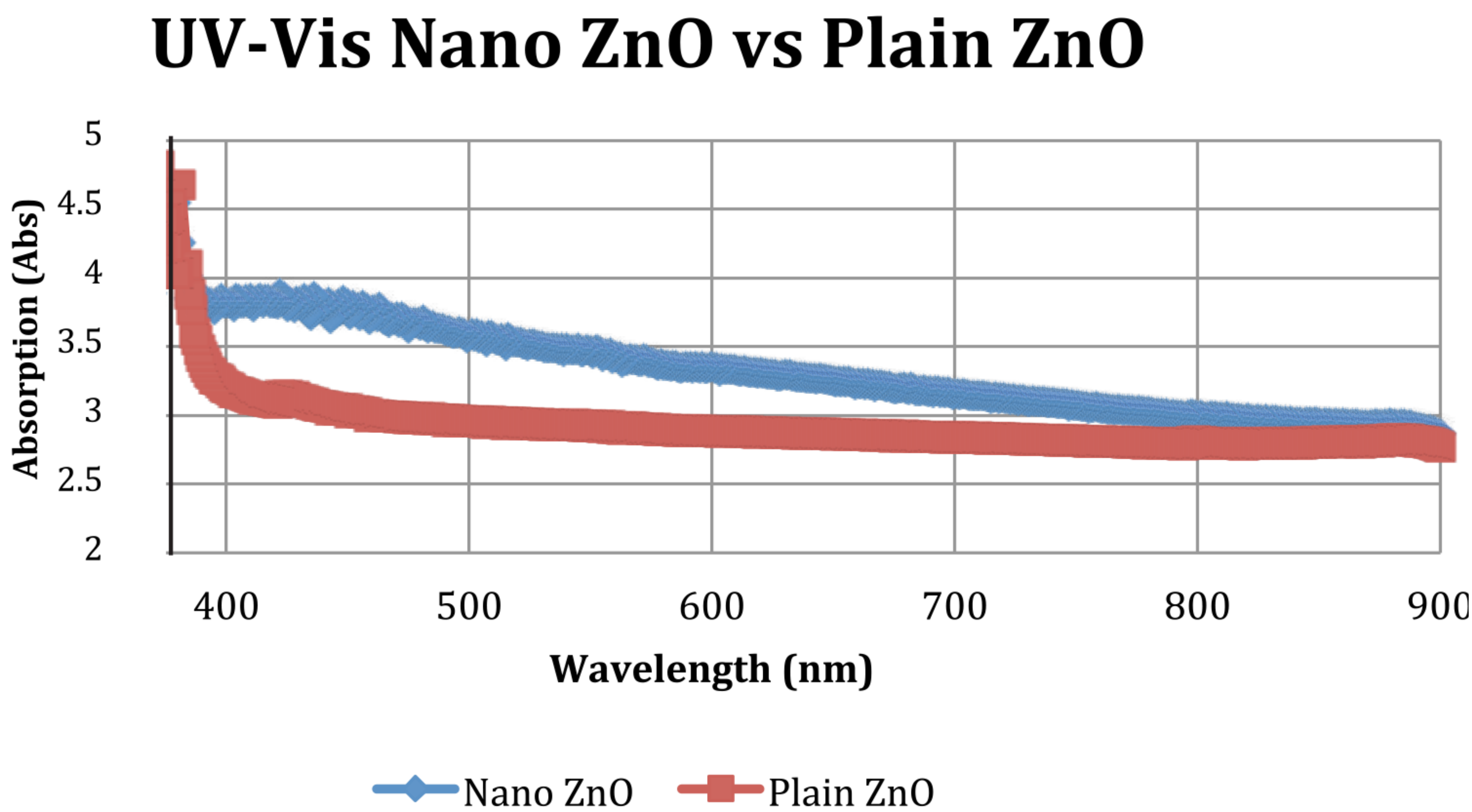
Best ZnO ink (#4)


Resistance after Sintering
Resistance (MΩ)
6
5
4
3
2
1
0
Immidiate
After 2 mins
After 4 mins
Nano ZnO Ink
Best Trial

Nano Ag Doping



Nano Ag Doping



Conclusions

- Various solvent based ZnO inks were formulated, gravure printed, sintered by photonic curing and tested for semiconductive behavior.
- Aluminum doped ZnO inks burned after sintering, and did not show semi conductive behavior.
- Lower screen ruling of the gravure image carrier exhibited better printing capability and more uniform spreading of ink film.

Conclusion cont…

- Nano ZnO inks utilized significantly lower amount of energy in photonic curing than ZnO w 1 micron particle size.
- Only silver doped ZnO inks demonstrated significantly increased absorption in the visible spectrum at 400 – 450 nm, showing semi conductive behavior.
- Doping with silver reduced the band gap of ZnO, and enhanced its semi conductivity.

Thank you!
Questions?

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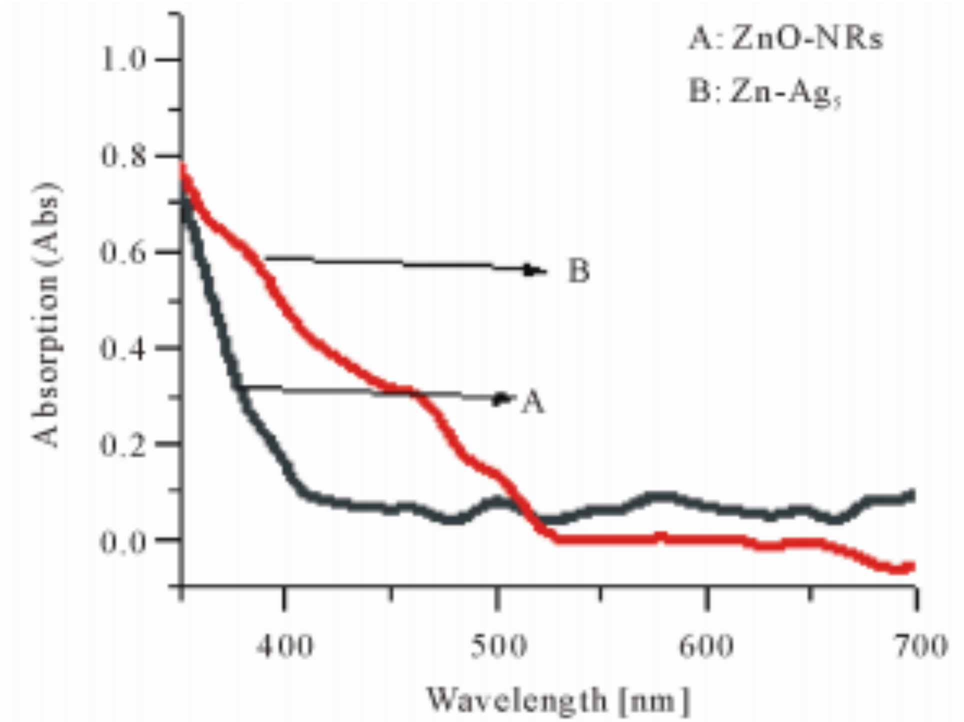
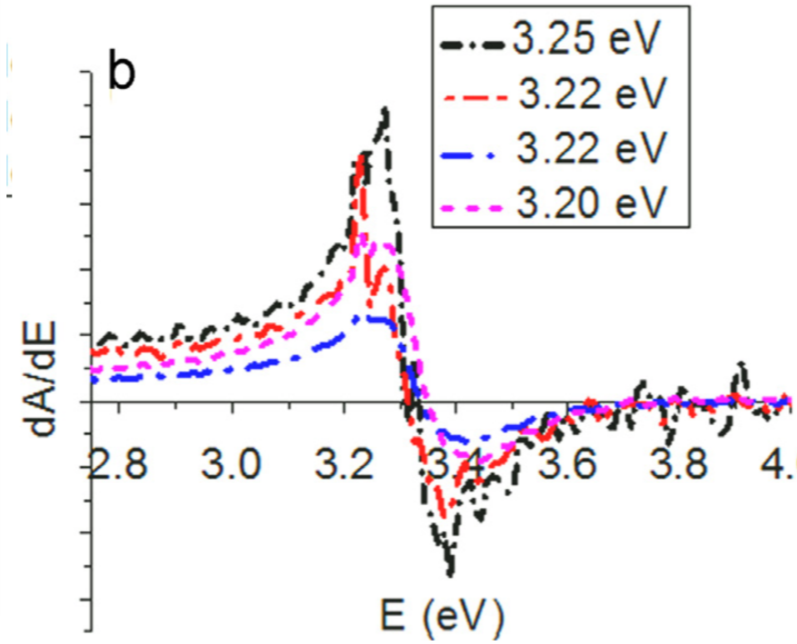
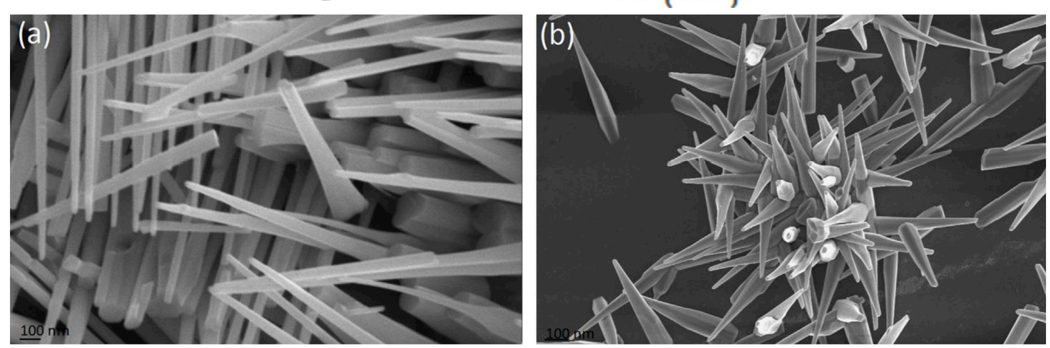
UV Spectra of ZnO Nanorods vs Ag Doped Nanorods







N.V. Nghia et al: “Preparation and Characterization of Silver Doped ZnO Nanostructures”. Open Journal of Synthesis Theory and Applications, 2012, pp. 18 – 22