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Synthesis of *fcc*-Metal Precursors and Nanoparticles for Radiation Hard Electronics

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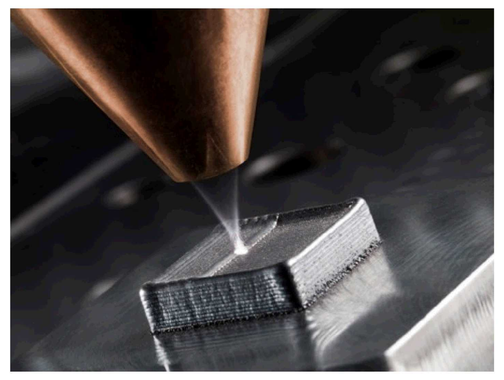
Introduction



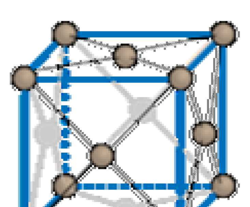
Copper costs $0.0074/gram

The demand for higher efficiency and smaller electronics continues to grow. As such, the demand for a new generation of materials that can meet these needs also increases. Nanometals have come to the forefront in electronic applications due to ability to be printed and sintered at the required smaller dimensions. Of these metals, the face centered cubic (*fcc*) structure copper has been presented as a lower cost alternative to more expensive materials (i.e., silver and gold) and fine controlled printing of circuits has been realized.

However, copper (and most metals) is susceptible to radiation damage, rendering them unusable in aerospace equipment, fighter jets, and weapon systems. In order to enhance the radiation stability of the nanoinks (N-inks) and develop radiation resistant printed materials, it was reasoned that doping copper with other metals may assist in stabilizing these materials to radiation damage. To accomplish this, nanocopper alloys were produced and tested for stability to radiation environments.

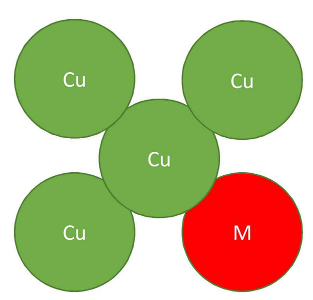
A variety of nano-*fcc*-metals including platinum, gold, silver, iron, and cobalt (bismuth was also investigated due to its high Z) were synthesized and used as dopants in a nanocopper ink. The syntheses, characterization, and ink formulations of the *in situ* and *ex situ* nanoalloys will be presented. Additionally, the printed traces were analyzed before and after ion irradiation to determine any impact radiation might have on these traces. The results from these studies will be presented.

Face-Centered-Cubic Metals

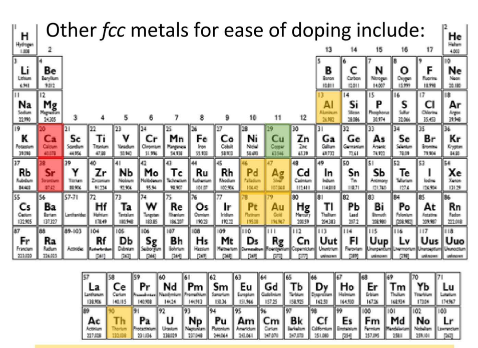


Cubic face centered (fcc)

Face-centered cubic (fcc or cF**)** refers to a crystal **structure** consisting of an atom at each cube corner and an atom in the center of each cube face.



Simplified schematic of a copper lattice doped with another fcc metal.



There are a variety of different fcc metals across the periodic table that will allow us to investigate different copper alloy prints.

FCC Metals Investigated

M: **Ca** – T. Nguyen
Sr – T. Nguyen
Ni – A. Vallejos
Pt – F. Guerrero
Au – N. Padilla
Pd – N. Padilla
Ag - X. Robinson
Th – X. Robinson
Al – P. Reuel
Bi – M. Ringgold

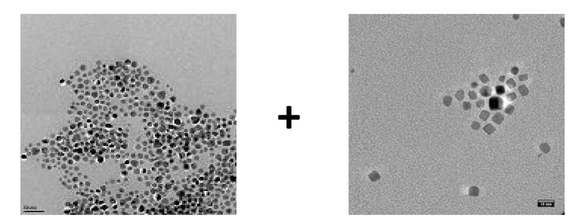
Each member was assigned a nano-metal dopant. The task was then to synthesize the nanoparticles and characterize them using TEM, PXRD, and XRF before formulating the ink

Two methods for alloy synthesis

Ex-Situ

This method involves taking both nanomaterials into an ink solution after synthesizing them individually

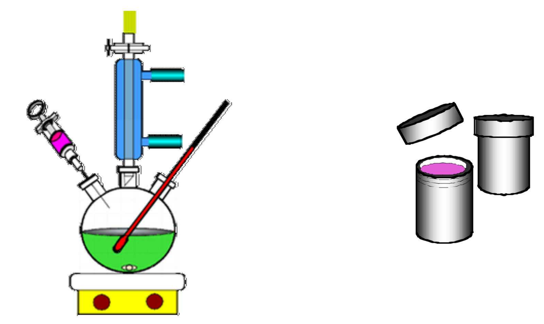
90% Cu°NP + 10% M°NP ⟶ CuM°NP



In-Situ

This method involves taking both nanomaterials into an ink solution after synthesizing them individually

90% CuMes + 10% Metal Precursor ⟶ CuM°NP

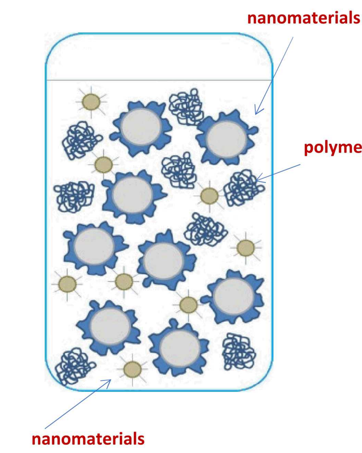


N-ink Formulation

Ink Systems are formed from multiple components:

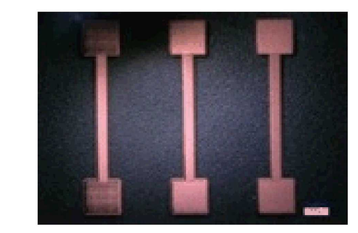
- Solvents (s), wetting agents, soluble polymers or micelles, & nanoparticle(s)
- Control over viscosity, surface tension, drying rate, and wetting are required.

H.C. Nallan et al. *Langmuir* **30** (2014) 13470.
R. Guo et al. *JECerS* **23** (2003) 115-122.
X. Zhao, et al. *Ceram.Intl.* **29** (2003) 887-892



A general approach for both *in-situ* and *ex-situ* nano-ink formulations:

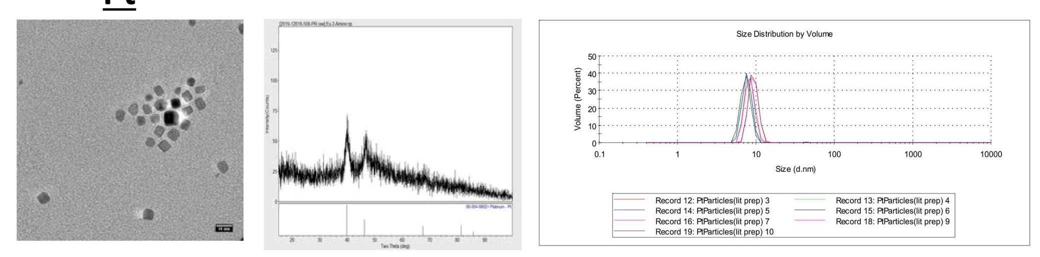
- Cu^0 and M^0 particles were combined at a 10% M^0 concentration.
- dissolved in a 4:1 vol/vol mixture of xylenes and White Spirits at a concentration of 4 g of the mixture to 1 g of the particles.
- sonicated until solution becomes smooth and homogenous.



FCC Metal Nanoparticle Overview

Pt

$$Pt(acac)_2 \xrightarrow[\text{ON/Oleylamine/OA, Fe(CO)}_5]{\text{1 hr at 200°C}} Pt^0$$

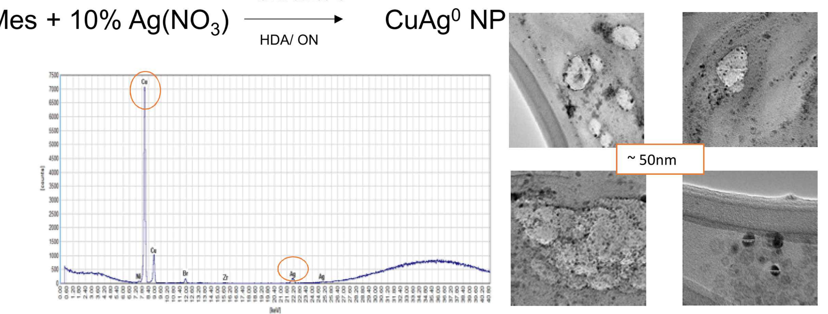


Synthesis of homogenous sub 10 nm Pt particles was successful

Ag

$$90\%\ CuMes + 10\%\ Ag(NO_3) \xrightarrow[\text{HDA/ ON}]{\text{1/2 hr at 250°C}} CuAg^0\ NP$$

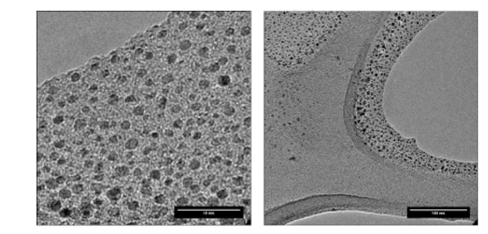
- CuAg nanoparticles are crystalline and are ~50 nm in size.
- Small amounts of Br is detected by XRF



Au

$$90\%\ CuMes + 10\%\ AuCl_3 \longrightarrow CuAu^0\ NP$$

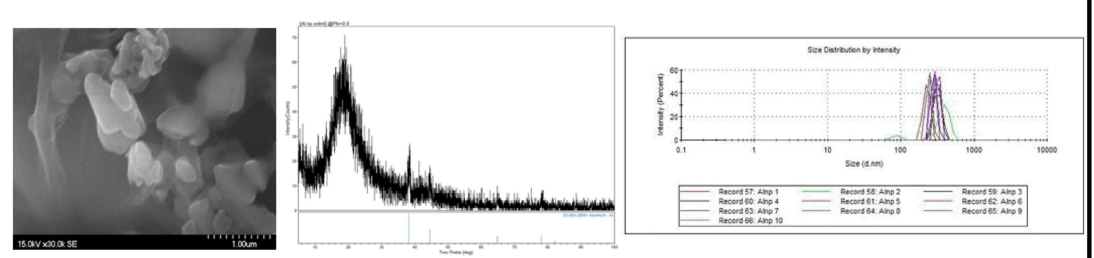
- HDA and $AuCl_3$ were heated to 300°C yielding a red solution.
- CuMes and ON were stirred together to form a brown-yellow slurry.
- The CuMes/ON slurry was quickly added to this heated solution to avoid oxygen exposure.



TEM of *in-situ* CuAu materials show a homogenous mixture of nanoparticles about 10 nm in size

Al

$$Al(acac)_3 + 3LiAlH_4 \xrightarrow[\text{reflux, 72 h}]{\text{mesitylene, 164 °C}} 4Al + H_2 + \text{other side products}$$

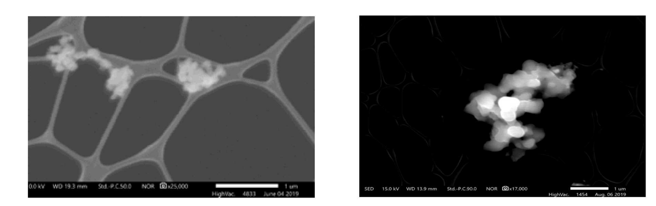


PXRD analysis showed presence of crystalline aluminum

Bi

A variety of bismuth precursors including halides, mesityls, and amides were reduced through acid digestion vessels at varying concentrations along with different surfactants.

PXRD, XRD confirm Bi(0) formed



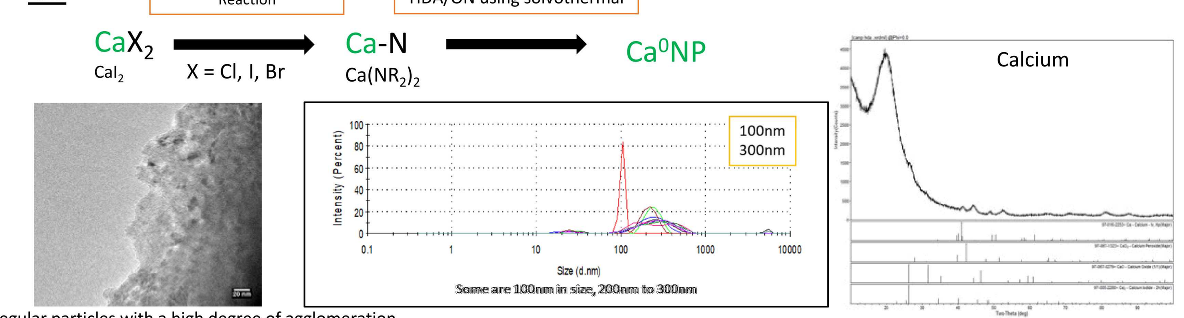
$BiMes_2Cl$ with ON at 180^0 C

$BiCl_3$ with LiNapth and THF at RT

Ca

Double Replacement Reaction; Convert to Nano with HDA/ON using solvothermal

$$CaX_2\ (CaI_2) \xrightarrow{X = Cl,\ I,\ Br} Ca\text{-}N\ (Ca(NR_2)_2) \longrightarrow Ca^0NP$$



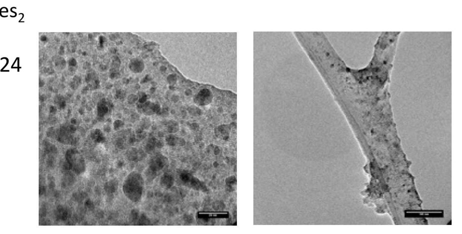
Irregular particles with a high degree of agglomeration

Sr

Double Replacement Reaction; Convert to Nano with HDA/ON using solvothermal

$$SrX_2\ (SrI_2) \xrightarrow{X = Cl,\ I,\ Br} Sr\text{-}C\ (SrMes_2) \longrightarrow Sr^0NP$$

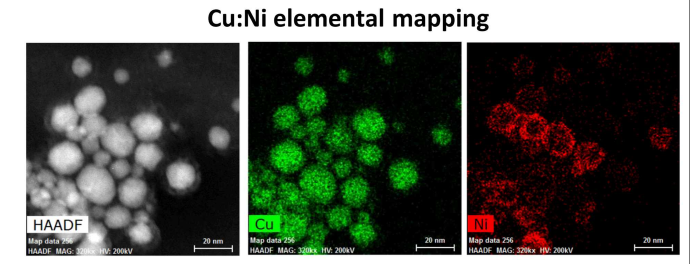
- Acid digestion vessel was heated to 180^0 C for 24 hr
- washed twice with hexane and toluene
- TEM of SrCu particles generated *in-situ* show irregular particle morphologies



Ni

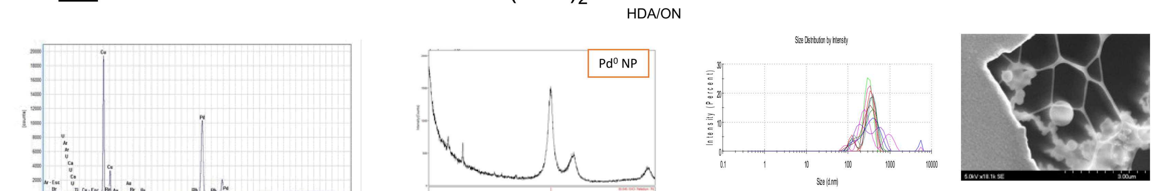
- CuNi nanomaterials were synthesized via microwave processes
- Elemental mapping of particles shows core/shell materials were produced
- Cu core
- Ni shell

Cu:Ni elemental mapping



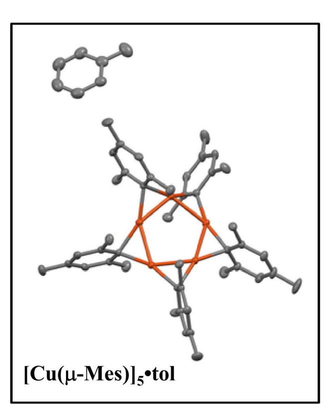
Pd

$$90\%\ CuMes + 10\%\ Pd(OAc)_2 \xrightarrow[\text{HDA/ON}]{\text{1/2 hr at 250°C}} CuPd^0\ NP$$

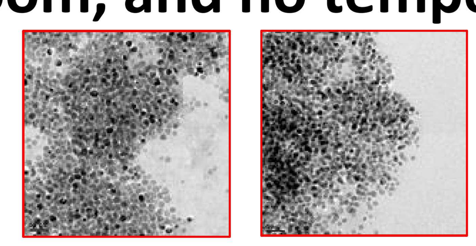


- XRF: CuPd w/ trace amounts of Br.
- PXRD shows crystalline Pd NP.
- DLS and SEM shows sample vary from 80-1000 nm

Synthesis of Copper Nanoparticles at high, low, room, and no temperature



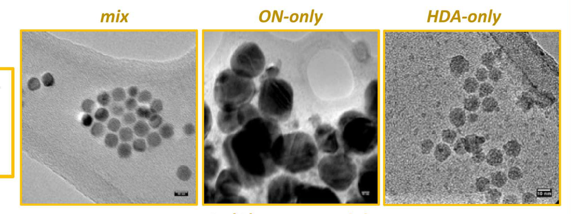
The synthesis of copper nanoparticles from copper mesityl has been realized using a variety of techniques and methods at varying temperatures.



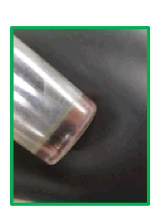
Cu(0) nanoparticles

High Temp: The synthesis of copper nanoparticles has been successful at a high temperature. This reduction is performed at 300^0 C in hexadecylamine and octylamine. Typically yields are ~2 g per batch.

Low Temp: Large scale synthesis (~ 100 g) of copper nanoparticles has also been realized generating homogenous particles of the same size at 180^0 C



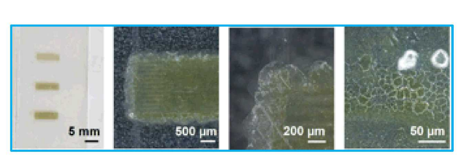
Cu(0) nanoparticles



Cu(0) nanoparticles

Room Temp: Small scale attempts at the reduction of copper nanoparticles at room temperature or near room temperature have been successful using amine reductants

No Temp: The copper mesityl precursor was printed directly onto the substrate and converted to metal using laser processing



CuMes direct print of Cu(0)

Printing

Once an ink was developed, it was transferred from the glovebox to be printed

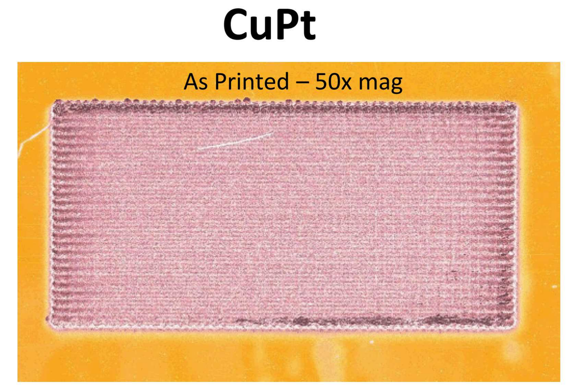
Printing

- Printed on Optomec M3D using Nitrogen carrier gas
- 34-38 ccm Sheath gas flow, 14-18 ccm Aerosol gas flow, 42-48 V atomizer voltage
- Print speed: 4 mm/s
- Printed 1, 2, 3, 4, and 5 layer 2 mm x 4 mm pads on 3 mil Kapton

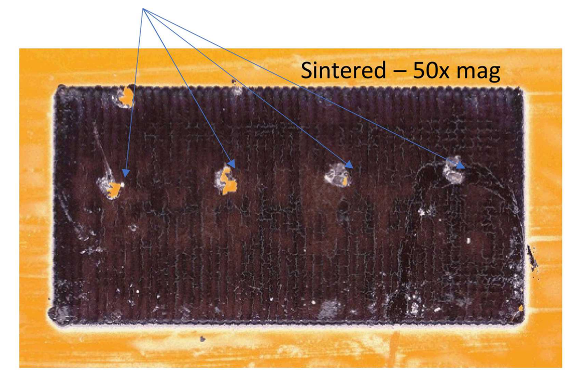
Sintering

- Sintered in tube furnace under 2.9% hydrogen balance argon at 375^0 C for one hour

CuPt



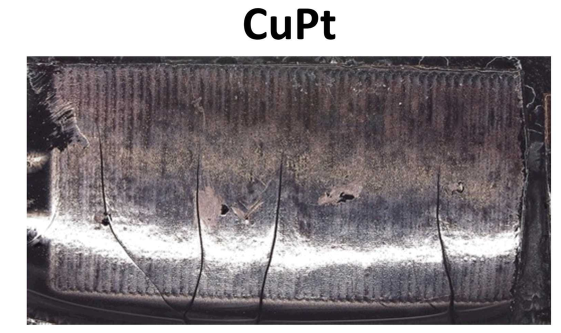
From 4 point resistivity measurement



Ion Beam

- Ion beam proved to be a challenge in exposing the prints to ion impact with consistency.
- The process of coating the prints with graphene as a part of the procedure for ion beam skews the conductivity measurements as the graphene itself is conductive.
- Identifying the location of the ionization proved difficult

CuPt



- In the future samples will be taken to the Gamma Irradiation Facility (GIF) so that the entirety of the print can be exposed to ion impact using a Co^{60} source.

Summary

The mixed alloys are being investigated for the proposed RAD stability but additional results are anticipated from these syntheses. RAD stability hard to determine due to IB carbonization for imaging/processing.

A. New precursors, surfactants
B. New materials, routes, properties
C. N-inks progress
D. Printing of alloys
E. Ion Beam exposure

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