# Formation and Characterization of Core Shell Structures on Nanoporous Gold

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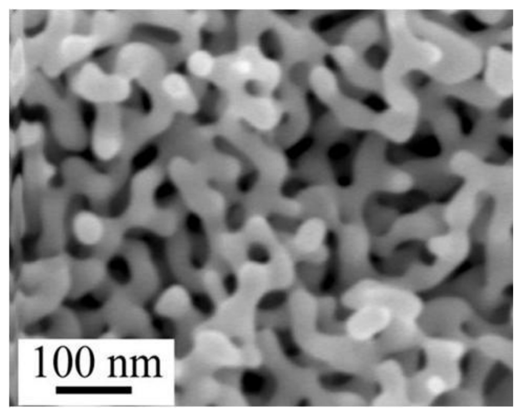
## Nanomaterials

- Becoming widely used in the world of developing technology
- Still much unknown about them
- Developing ways to improve or modify their characteristics
- Nanoporous gold (NPG)is one nanomaterial that is used but has downfalls
- Reported hardness is 145 Mpa [1], however the material as a whole is brittle and difficult to work with
- Great characteristic is the large surface area on a small volume
- Large surface area is a result of the network of tunnels and pores



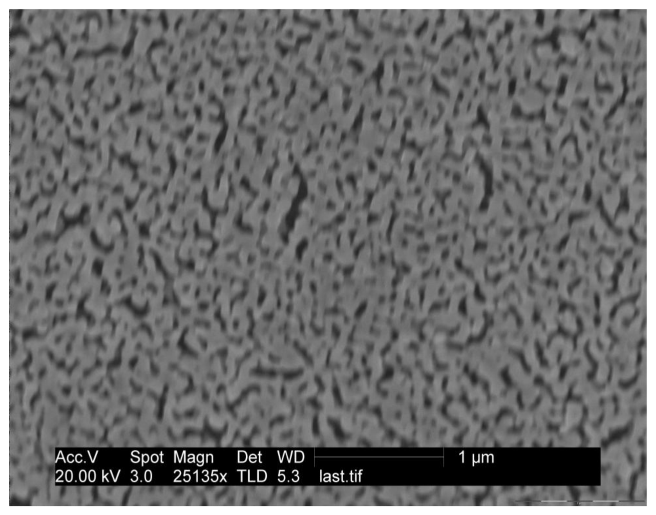
NPG foam [2]

## Nanoporous Gold

Widely produced in either a foam of film form, NPG is created by dealloying a commonly produced gold and silver compound. For this specific project, the gold was 30.5% at. The dealloying process, as performed by T.J. Balk[3], uses nitric acid to dissolve the silver out of the unprocessed gold. This leaves tunnels of pores and ligaments which resemble a sponge. The average size of the pores is 57 nm, while the ligament average is 63 nm.

## Objective

Work has been done with plating thin films into NPG, but performance for catalysis was the focus. In this project, the hardness of plain NPG was measured and as well as NPG with the addition of other metals. Forming a core shell structure from the NPG allows for varying thicknesses, differing metals, and potential layering. Nickel and gold were both chosen, as nickel is often worked with gold. The choice of gold kept p the chemistry of the NPG the same while only changing a physical characteristics.

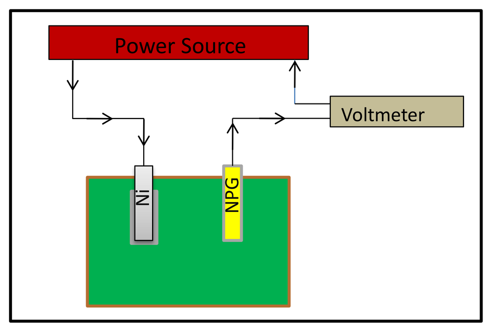

300 nm dealloyed gold – basis for plating

## Methods

To obtain a layer of nickel on the NPG, electroplating in a Watts bath was the best choice. Electroless plating was chosen to fabricate the layer of gold. A scanning electron microscope (SEM) took photos of the NPG before and after plating. A nanoindenter performed a series of indents on each sample to determine the hardness. Finally, an EDX test was also run to determine the chemistry of the nickel plated NPG for reference.

## Electroplating

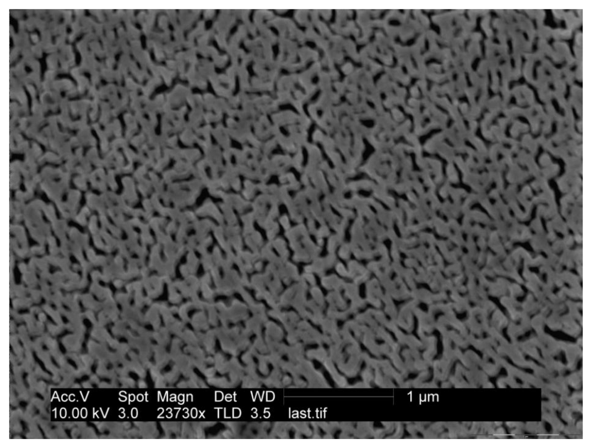
A 250 mL Watts bath consisting of 48 g Nickel Sulfate, 6 g Nickel Chloride, and 6 g Boric Acid [4] plated the NPG with nickel. Kept at a constant temperature of 58° C, the voltage varied to achieve the desired current in the calculated time. A nickel rod acted as the cathode. Because electroplating can sometimes not be as uniform as electroless, the method was changed for gold plating.

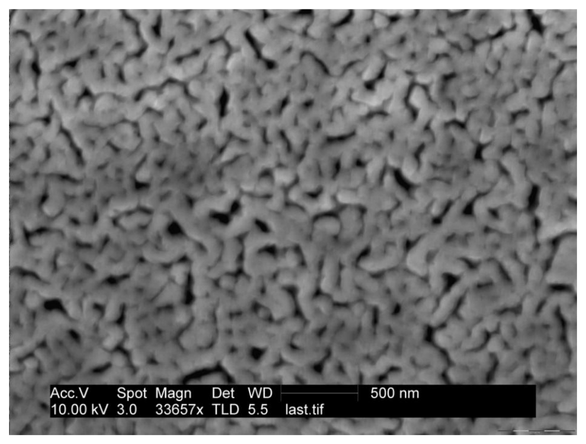


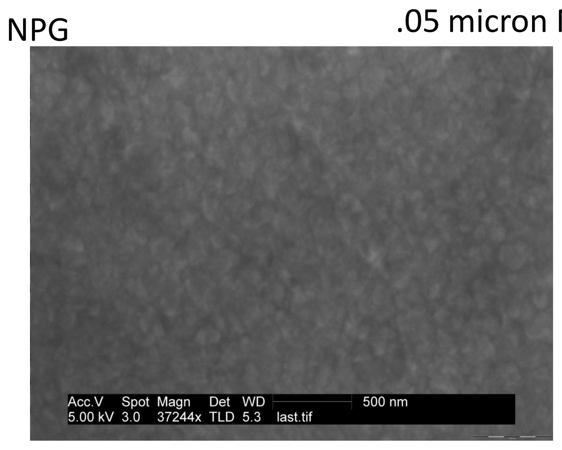
Schematic of electroplating setup

| Thickness | Current Density | Area | Current | Time |
|---|---|---|---|---|
| 0.016 microns | 5 A/dm² | 0.21 cm² | 10.5 mA | 1 s |
| 0.05 microns | 5 A/dm² | 0.28 cm² | 14 mA | 3 s |
| 0.5 microns* | 0.5 A/dm² | 0.18 cm² | 9 mA | 30 s |

Experimental specifications for electroplating
*.05 microns plated for visual comparison only

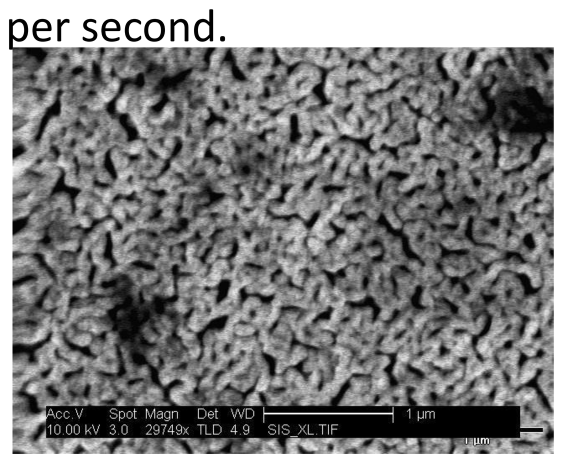

.016 micron Ni-plated NPG

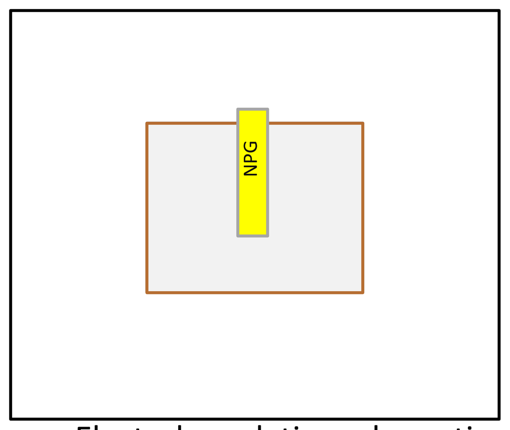

.05 micron Ni-plated NPG


0.5 microns Ni-plated NPG

## Electroless Plating

Electroless plating utilized a gold electroless solution of 3.7 g/L Au. The necessary requirement of temperature, 71°C was met with a calculated time of 3 minutes for plating. Time was calculated from a given deposition rate of $1.1 \times 10^{-4}$ microns per second.


0.3 micron Au-plated NPG



Electroless plating schematic

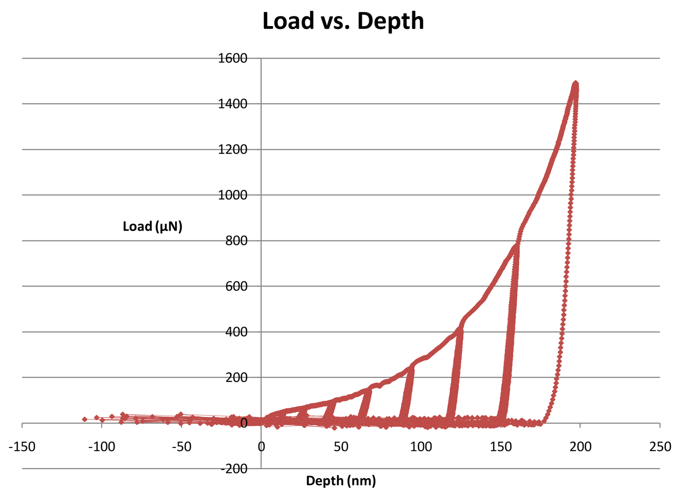
## Nanoindentation Testing

A series of indentations was performed on each of the four types of specimens: .016 microns NIi, .05 microns Ni, .03 microns Au, and unplated NPG. Indenting occurred on a Hysitron Nanoindenter, with a Nist Berkovich tip. Partial unloading from depths of 25-200 nm with ten steps gathered hardness data.

## Results

| Sample | Hardness | Ave. Pore Size | Ave. Ligament Size |
|---|---|---|---|
| NPG-plain | 0.576 GPa* | 57.03 nm | 63.37 nm |
| .016 micron Ni | 3.15 GPa | 52.93 nm | 66.94 nm |
| .05 micron Ni | 1.19 GPa | 45.40 nm | 88.71 nm |
| .03 micron Au | 1.03 GPa | 54.07 nm | 71.35 nm |

*Differs from published value



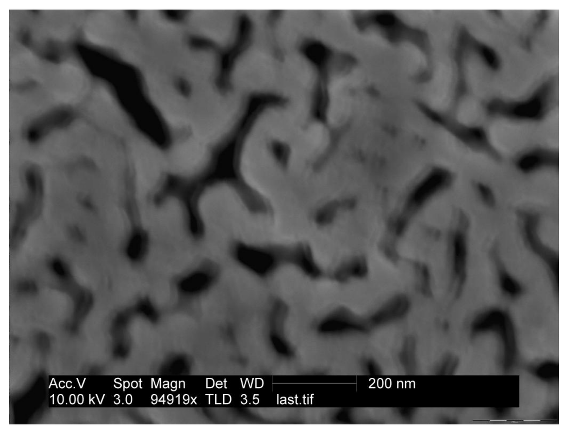
Load-Depth curve for NPG indent

| Element | Wt% | At% |
|---|---|---|
| O K | 01.39 | 06.29 |
| SiK | 20.35 | 52.36 |
| AgL | 02.28 | 01.53 |
| NiK | 13.83 | 17.02 |
| AuL | 62.14 | 22.80 |

Results of EDX composition test

## Conclusion

The plating significantly increased hardness as compared to the unplated NPG. The nickel samples were harder than the gold plated and unplated specimens, supporting the claim that changing the chemistry of the compound increases hardness. The addition of the layer of nickel changed the NPG from a single to a polycrystalline structure, which would be an explanation for the increase in hardness. Changing the thickness of the ligaments also increases hardness, based on the Au-plated data. The EDX composition further demonstrates the changing of chemistry and affirming the plating of nickel onto the NPG.


Close-up of 0.16 micron Ni-plated NPG

## Future Work

It is not clear which affects hardness more, chemistry or thickness of ligaments; further testing should prove or disprove these findings. Generating photos and measurements from cross-sectional areas will determine whether or not the plated layer followed the contours of the NPG and give a more accurate ligament size. A second layer plated onto the samples would vary data and possibly increase the hardness, though the more effective method of increasing hardness has not yet been determined.

## References

1. Hakamadaa M. , and Mabuchi M. (2007). Mechanical strength of nanoporous gold fabricated by dealloying. *Scripta Materialia*, *v. 56*(11), 1003-1006.
2. Hodge, A.M., Hayes, J.R.,Caro, J.A., Biener, J., Hamza, A.V. (2006). Characterization and mechanical behavior of nanoporous gold. *Advanced Engineering Materials, v*. 8 (9), 853 - 857.
3. Sun, Y., Ye, J., Minor, A.M., Balk, T.J. (2009). In situ indentation of nanoporous gold thin films in the transmission electron microscope. *Microscopy Research and Technique, v*. 72 (3), 232-241.
4. Dennis, J.K., and Such, T.E. 1972. Electroplating baths and anodes used for industrial nickel deposition, *Nickel and Chromium Plating, Butterworths and Co., Cambridge, 2nd ed., p. 36-54.*

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