Multivariable Analysis of Hard Anodization

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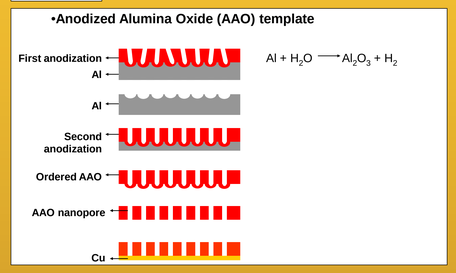
Motivation

•Anodized Aluminum Oxide (AAO) nanopores are used as molds in the electrodeposition of metal nanowires.
•The diameter of the pores can greatly affect the wires' properties

The Hard Anodization (HA) method was employed:
•Higher 2nd Anodization voltage
- Faster sample production.

•The 1st and 2nd anodization steps were analyzed:
- Powerful effect on diameter
- Relative lack of understanding of their effect with HA

Figure 1:



Experiment

Five parameters were tested:
•1st Anodization Voltage (V_1) and Temperature (T_1)
•2nd Anodization Voltage (V_2) and Temperature (T_2)
•Concentration (C) of the oxalic acid bath

The Taguchi method for design of experiments was employed:
•Analyze multiple variables at once.
•Only 16 trials, each with a specific combination of variable levels.
•Not accurate, but gives a general impression of each variable's effect. Table 1 lists the combinations for each trial.

Trial procedure:
•One-hour 1st anodization, at the prescribed voltage, temperature, and concentration.
•One-hour oxide etch, in a 65ºC phosphoric-chromic acid mix.
•1-3-hour 2nd anodization, at the prescribed voltage, temperature, and concentration.
•Metal-coated pieces of each sample to reduce charging in the SEM
•Measured pore diameters manually in an SEM.
- Used the microscope software's annotation tool to manually measure multiple pores, as shown in Figure 7.
- Took the average of those measurements as the pore diameter for that sample.

If the Taguchi data did not yield an easy formula, a 4-trial run would be performed, analyzing only the most linear variable with a satisfactorily large range.

Table 1:

Sample #	V1 (V)	T1 (°C)	V2	T2	C (M)	Averages:
1	20	1	47	1	0.2	21.12857
2	20	7	53	7	0.3	21.3625
3	20	13	60	13	0.4	27.26538
4	20	17	65	17	0.5	28.33125
5	30	1	53	13	0.5	
6	30	7	47	17	0.4	31.21333
7	30	13	65	1	0.3	22.92
8	30	17	60	7	0.2	21.87143
9	40	1	60	17	0.3	29.6
10	40	7	65	13	0.2	25.54706
11	40	13	47	7	0.5	27.47619
12	40	17	53	1	0.4	21.43125
13	50	1	65	7	0.4	27.83636
14	50	7	60	1	0.5	
15	50	13	53	17	0.2	37.44118
16	50	17	47	13	0.3	39.41667

Figure 2:

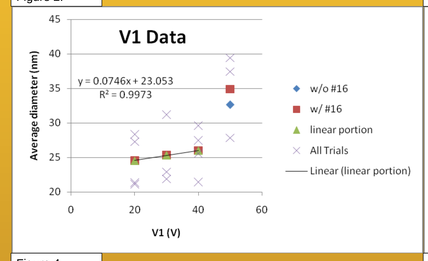


Figure 3:

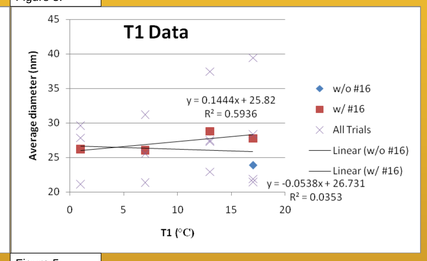


Figure 4:

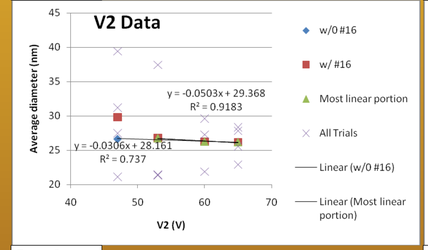


Figure 5:

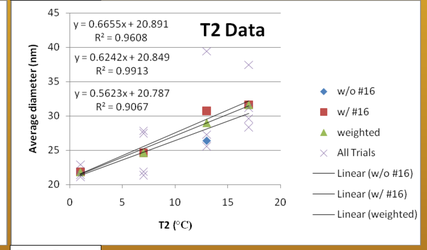


Figure 6:

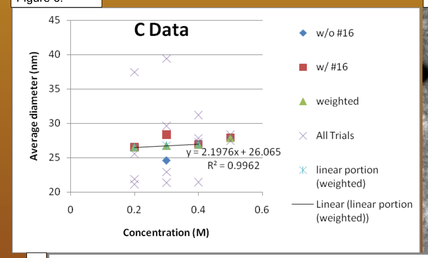


Figure 7:

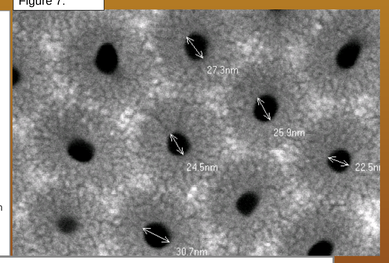
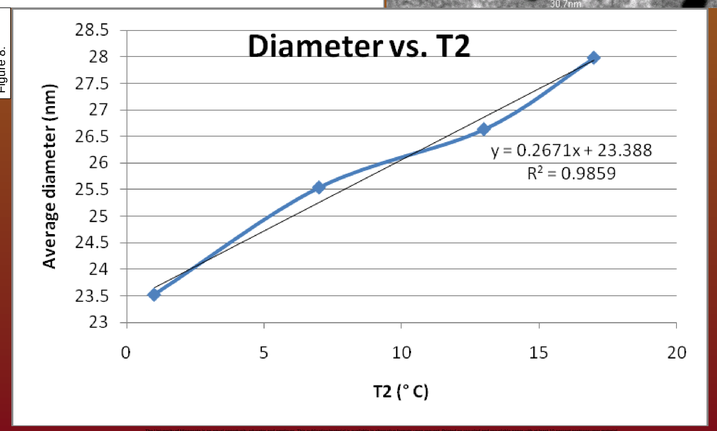


Figure 8:



Results

•Raw Taguchi trial results are presented in Table 1.
•Three anomalies:
- #5 and #14 produced no results at all
  - 0.5M oxalic acid precipitates above 1ºC
- #16 had severely deformed pores, possibly due to V_2 being smaller than V_1
  - Still had measureable diameters
  - Seemed to improve linearity of the Taguchi data if taken into account at full or half weight.

•Taguchi factorial effects for each variable are shown in Figures 2-6
- V_1, V_2, and T_2 showed linear behavior for at least three consecutive levels
- Only T_2's effect was linear over entire range of levels, and had the widest range of all the effects, about 21-31nm

•Examined T_2 in a single variable, four-trial run
- Other four variables set to V_1=40V, T_1=1ºC, V_2=60V, and C=0.3M.
- Varied T_2 at previously used levels: 1ºC, 7ºC, 13ºC, 17ºC
- Resulting data in Figure 8 ranges from ~23.5nm to ~28nm
  - Highly linear

Conclusions

•The Taguchi trials were a partial success.
- Three of the variables showed some linear behavior.
- However, T_1 and C showed little to no linearity.
  - Could not get a linear formula of all five variables.

•The T_2–only trial run proved more successful.
- Results ranged from 23.5-28, about half the range expected.
- However, the resulting formula d(nm) = 0.2671*T_2(ºC) + 23.388 has good precision.
  - Should be able to use T_2 for fine control of pore diameter in later experiments.

References

•W. Lee, R. Ji, U. Goüsele, K. Nielsch, Nature Mater. **5**, 741 (2006).

•W. Lee, K. Schwirn, U Goüsele, Nature Mater. **3**, 234 (2008).

•Roy, Ranjit K., *A Primer on the Taguchi Method*. Van (1990) Nostrand Reinhold, New York, NY.