# Sputtering, Electrical Conductivity and Wet Etching of Molybdenum Films

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**Abstract:**

**The purpose of this study is to examine how certain parameters such as deposition rate, pressure, power, affect the resistivity of molybdenum when using the Angstrom Sputterer. For the purposes of this experiment, developing a film (~1000Å) with low resistivities is desirable (near bulk resistivity). In addition, a guide has been compiled for future clean room use that gives the characteristics of sputtering molybdenum on the DC1 source and the RF source.**

**Introduction:**

In many integrated circuits, depositing a metal layer on a substrate can be performed by thermal evaporation, electron beam evaporation, or sputtering. Molybdenum has a high melting point (2896 K) and a low vapor pressure (3.47 Pa at 3000 K) which makes molybdenum ideal for sputtering. For this reason, sputtered molybdenum sticks well to glass substrates, and the use of molybdenum can be commonly found on liquid crystal TFT displays as the gate metal on the TFT.

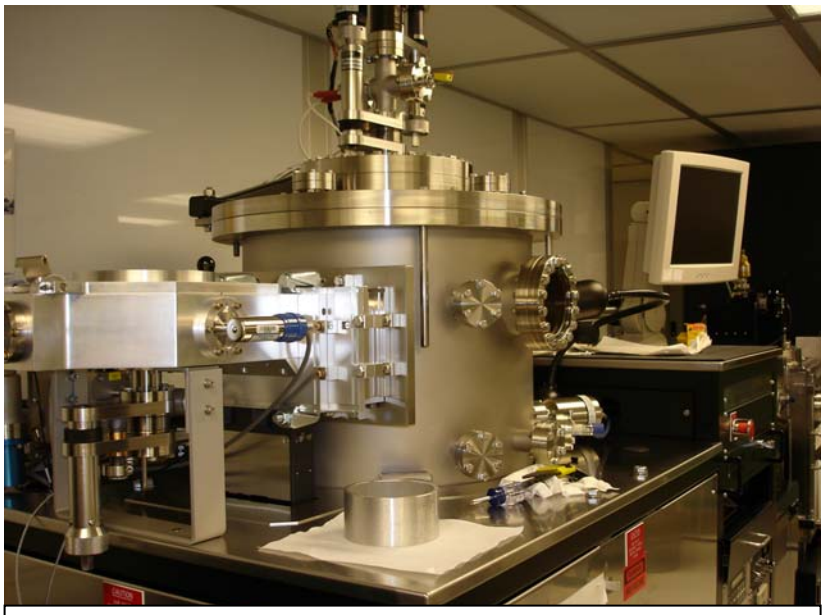
**Procedure:**

**Cleaning Glass Substrates**

Smooth glass slides need to be cleaned so no extraneous particles can collect on the surface. Glass slides are filled up on a plastic rack and placed into a metal container. Two drops of cleaning solution are applied to the slides and the metal container is filled with water. The slides are rinsed twice with DI water and the metal container is filled with DI water to approximately two inches below the brim. The slides are boiled at high temperature on a hot plate for about twenty minutes. After the boiling process, the slides are applied to an ultrasonic cleaner (Branson 3510). The slides are alternated between being boiled and being applied ultrasonic for three times. When the processes have completed, the slides are clean and ready to be used.

**Sputtering**

The molybdenum film is deposited by using the Angstrom Sputterer. The sputterer makes use of plasma, which contains electrons and ions in high energy states, to bombard the molybdenum atoms. The momentum of the ion bombardment dislodges the molybdenum atoms from the target, and the molybdenum atoms scatter in all directions. The dislodged molybdenum atoms come in contact with the substrate, which have enough energy to travel to and bond with the substrate.



Angstrom Sputterer

During experimentation, a clean glass slide is placed on a holding plate in the load lock. After the load lock is pumped down, the transfer arm is used to carry the plate from the load lock and into the main chamber. Once the transfer arm is removed and the valve to the load lock compartment is closed off, the plate is raised and positioned for sputtering.

Sputtering for the first time is preconditioned for 5 minutes. Deposition rate and power are variable while testing conditions in the DC1 source and RF source; preconditioning times, tooling factor, thickness, and substrate index are kept constant. The substrate index is variable when testing the effects of pressure on sputtering; all other parameters are kept constant.

Once sputtering is completed, the plate is lowered and the transfer arm is attached to the plate. The molybdenum deposited sample is taken out when the plate is back in the load lock.

**Photoresist and Etching**

The thickness of the molybdenum film is measured by applying a film of photoresist, etching the metal, and removing the photoresist. The sample is prebaked for about 5 minutes at 110 degrees Celsius. HMDS is applied to a portion of the surface, and AZ5214 (photoresist) is applied over the HMDS. Once the sample is softbaked for 1 minute at 95 degrees Celsius, the sample can be etched.

The molybdenum wet etching solution is made up of the following contents: 30 mL $H_3PO4$, 18 mL $HNO_3$, 10 mL $CH_3COOH$, 65 mL $H_2O$. The etch rate for this solution is approximately ~40 Å/s.

Once the molybdenum is etched, photoresist is removed by acetone and isopropyl alcohol and the sample is dried with an N2 gun.

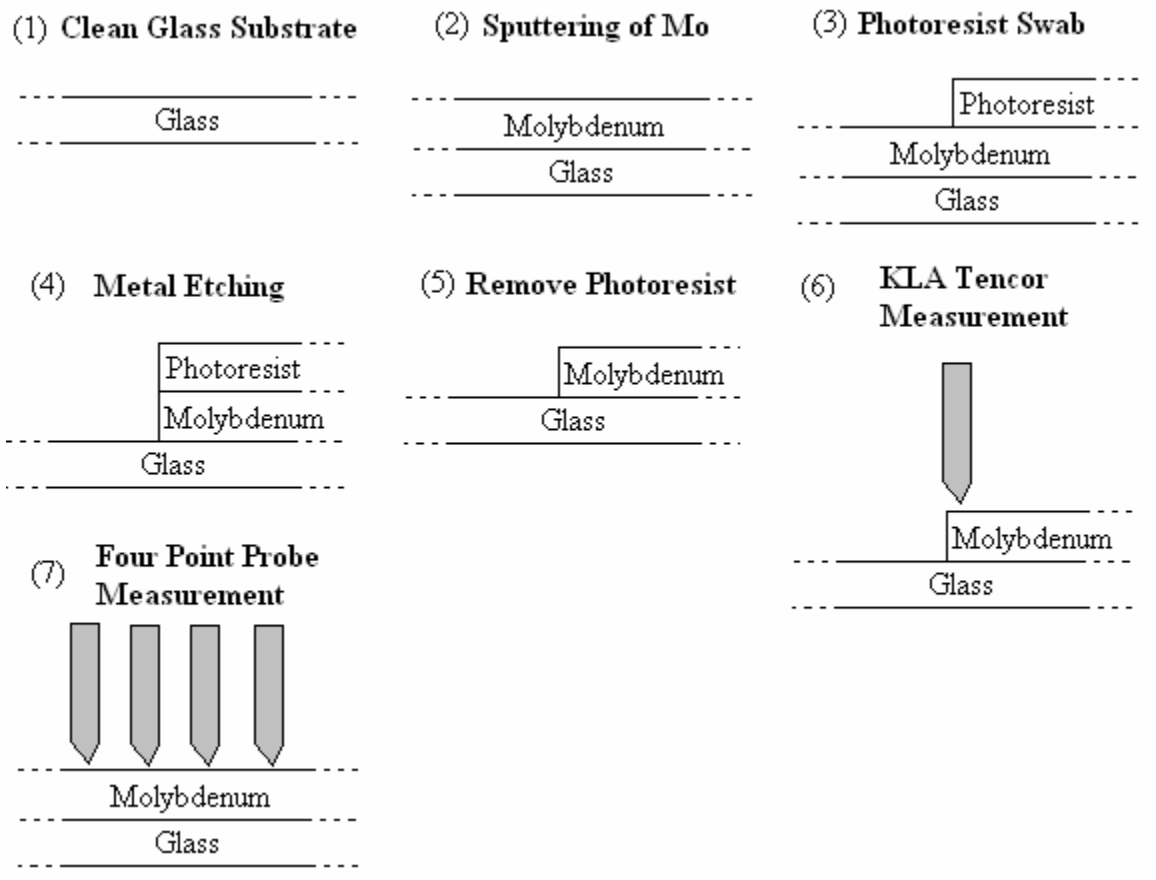
**Measurement**

The film is measured using the KLA Tencor P15 Surface Profiler. One use for measuring thickness is to correct the tooling factor for a first time use of the Angstrom Sputterer. All other measurements are used to verify the consistency of thickness by the sputterer.

The microhead of the KLA Tencor is brought to the edge of the surface for measurement where there is a plateau between the glass substrate and molybdenum film. Once the film is measured, the resistivity of the sample is found using a four point probe.

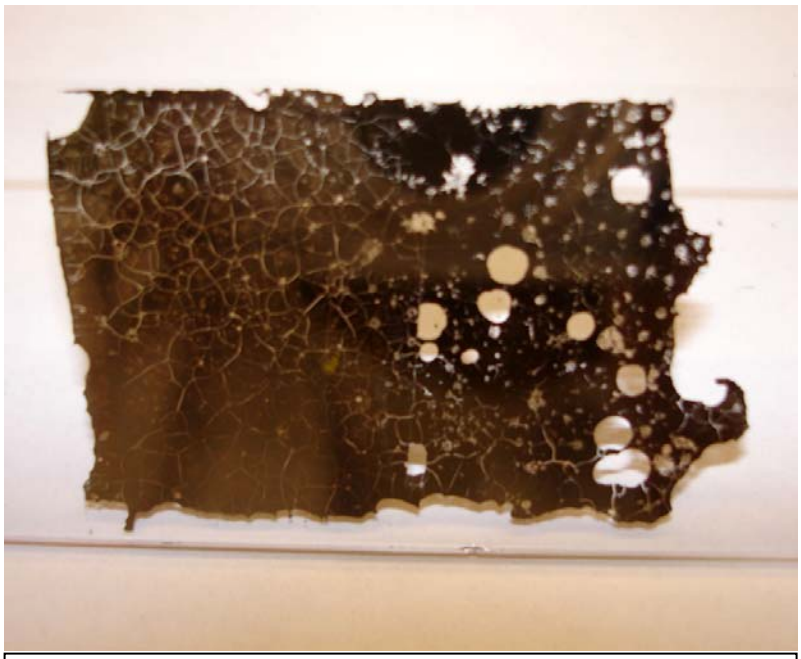
KLA Tencor P15 Surface Profiler

**Procedure Overview**



**Problems:**

Because there was no pre-made solution for molybdenum wet etching, several recipes had to be tested. The first recipe involved a combination of $H_2SO_4$, $HNO_3$, and water. The problem with this solution was that the etching was too fast and too strong (at a ratio of 5:3:2, respectively), and the first couple attempts showed that the solution actually penetrated through the photoresist layer. Even when the concentration of $H_2SO_4$ and $HNO_3$ were diluted by adding more water, the etching was still too fast for the purposes of this experiment.



Overetched Mo with $H_2SO_4$ : $HNO_3$ : $H_2O$, 5:3:2 ratio

Another attempt at etching the molybdenum involved using $H_3PO_4$, $HNO_3$, and water at a ratio of 10:15:100, respectively. This gave similar results when compared to the $H_2SO_4$, $HNO_3$, and water combination. The etching was still too fast.

The final attempt involved using $H_3PO_4$, $HNO_3$, $CH_3COOH$, and water. The initial ratio tested was 5:2:4:150, but the solution was too diluted, and the sample hardly etched after 5 minutes had passed. After multiple tries, a reasonable etch ratio was found:

30 mL $H_3PO_4$

18 mL $HNO_3$

10 mL $CH_3COOH$

65 mL $H_2O$

The etch rate for this solution was approximately ~40 Å/s. However, the solution often experienced an abnormally high etch rate for the first sample, but a consistent etch rate of ~40 Å/s for the subsequent etches.

An analysis of the etching was performed. Theoretically, the fast etch should provide a steep slope when the step is measured because the solution should etch directly into the molybdenum. In

order to compare first and second etches with the etch recipe above, two samples were used—both with similar thickness, deposition rate, and power. Plots of the first and second etches were obtained:

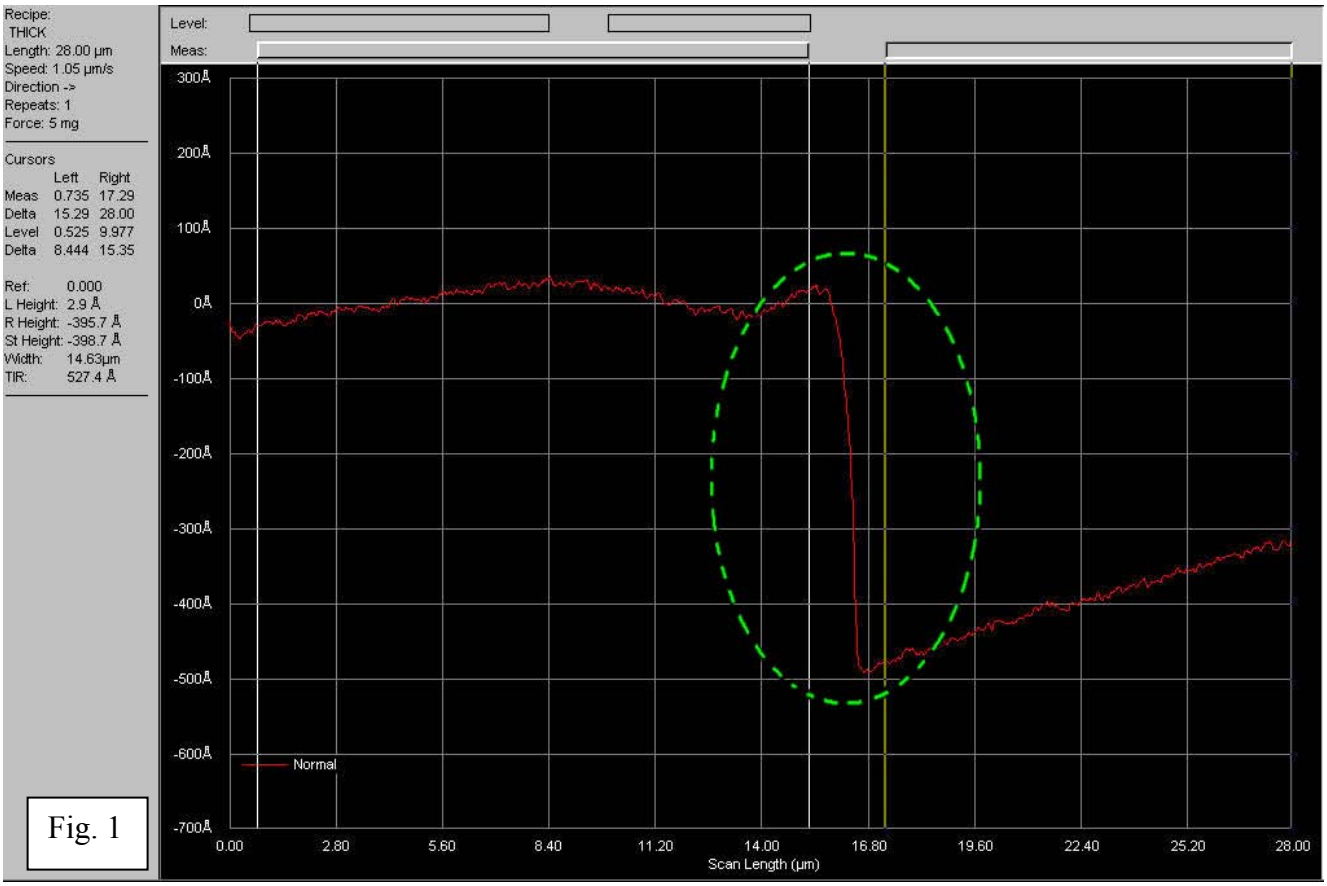



Fig. 1

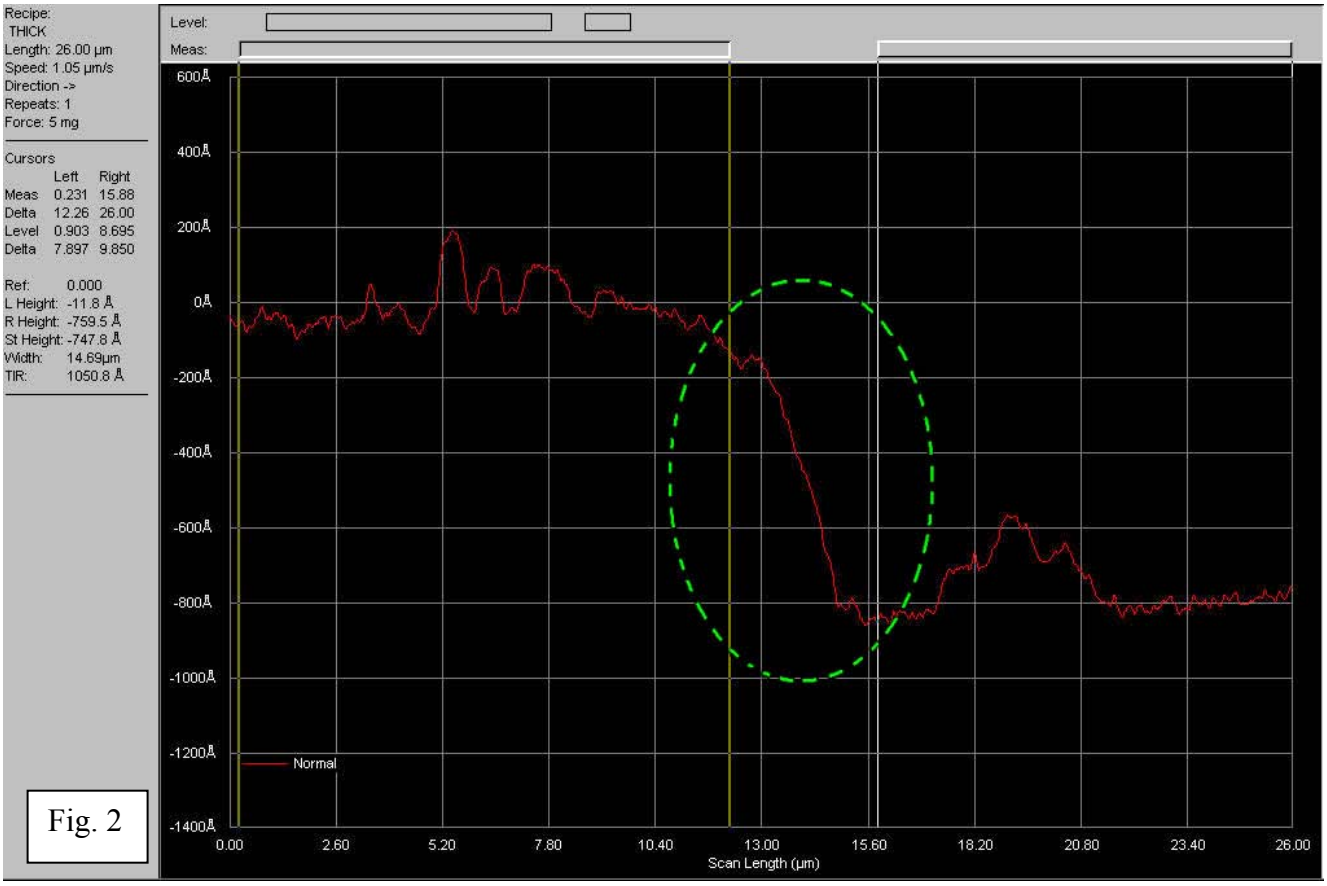



Fig. 2

The highlighted region shows the area of the step. Fig. 1 is the plot for the initial etch, and Fig. 2 is the plot for the second etch. The slope for Fig. 1 is approximately ~500Å / 1.4µm, or about 357.14 Å/µm, and the slope for Fig. 2 is approximately ~800Å / 2.6µm, or about 307.69 Å/µm. This shows that the first etch provides a significantly faster etch than the second etch. The slow etch provides more irregularities in the step because as the solution moves down from the molybdenum film towards the glass substrate, it will start to etch part of the molybdenum beneath the photoresist. This gives way to the sloped behavior, as evidenced in Fig. 2.

It is possible that the solution is not well blended when all the ingredients are mixed together—this may lead to a fast first etch. One possible solution to this problem is to stir the contents of the solution well before attempting to etch.

Besides the etching, the sputterer presented a few problems. Due to some unfortunate circumstances, the load lock valve opened while the base pressure was pumped down, forcing a clean room user to regenerate the sputterer anytime the target was changed. In addition, the load lock pump down and base chamber pump down were not very well coordinated, and it often took multiple tries to have the pressures in both the load lock and base chamber reach the same pressures.

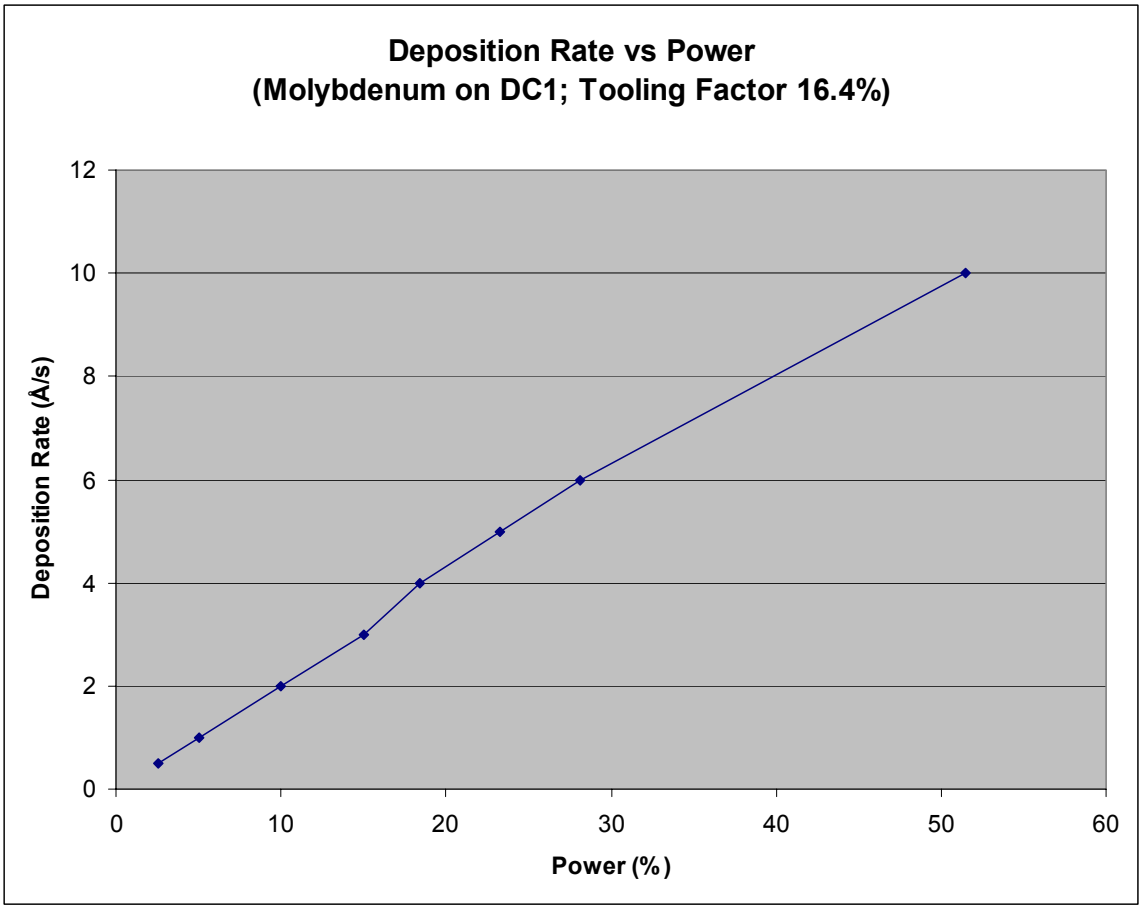
**Results:**

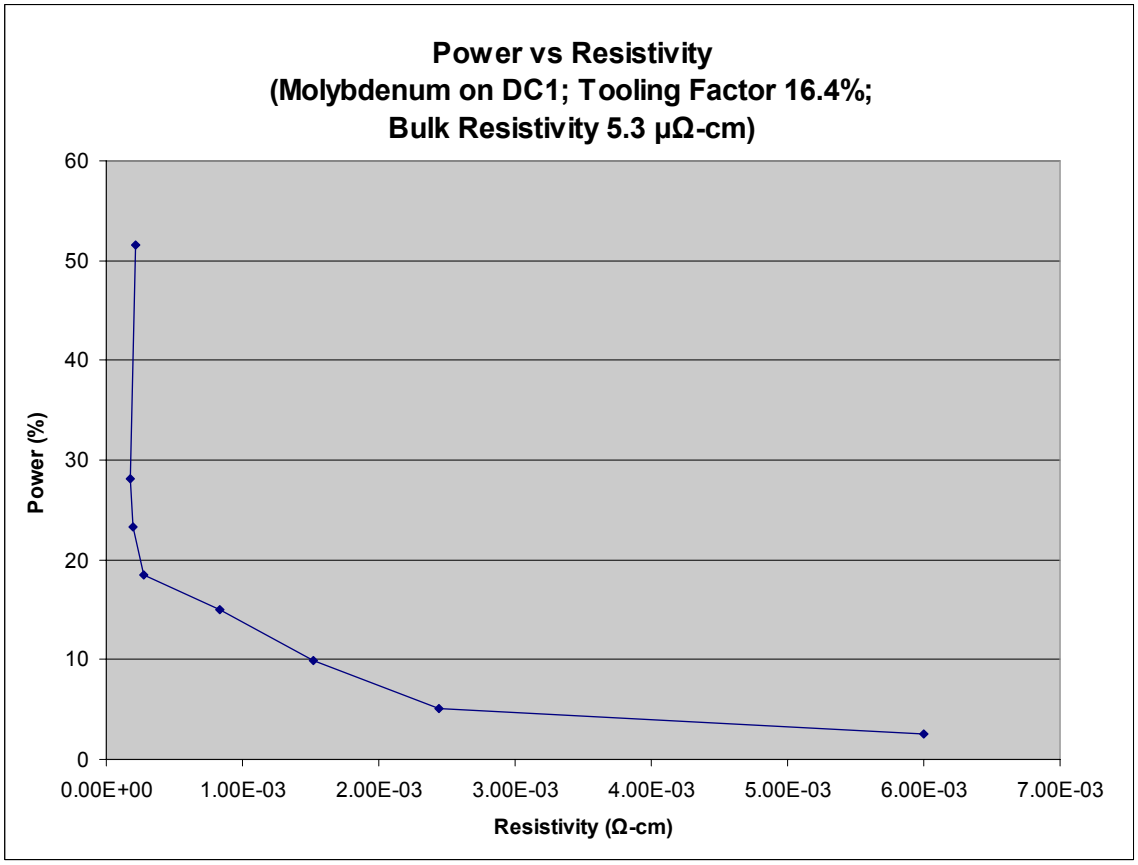
The first set of data was performed at a tooling factor of 16.4% at 10 mTorr. The following data is the information obtained through experimentation:

**Molybdenum on DC1; Tooling Factor: 16.4 %; Bulk Resistivity: 5.3 x $10^{-6}$ Ω-cm; Molybdenum Melting Point: 2896 K, Molybdenum film thickness ~1200 Å, Sputtering Pressure: 10 mTorr**

| | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 |
|---|---|---|---|---|---|
| Power (%) | 23.24 | 18.43 | 28.09 | 2.56 | 5.08 |
| Dep. Rate (Å/sec) | 5 | 4 | 6 | 0.5 | 1 |
| Four Point Probe Resistivity (Ω-cm) | $1.94 \times 10^{-4}$ | $2.71 \times 10^{-4}$ | $1.79 \times 10^{-4}$ | $6.00 \times 10^{-3}$ | $2.44 \times 10^{-3}$ |

| | Sample 6 | Sample 7 | Sample 8 |
|---|---|---|---|
| Power (%) | 51.5 | 9.96 | 15.03 |
| Dep. Rate (Å/sec) | 10 | 2 | 3 |
| Four Point Probe Resistivity (Ω-cm) | $2.18 \times 10^{-4}$ | $1.52 \times 10^{-3}$ | $8.33 \times 10^{-4}$ |


Deposition Rate vs Power
(Molybdenum on DC1; Tooling Factor 16.4%)
Deposition Rate (Å/s)
0
2
4
6
8
10
12
0
10
20
30
40
50
60
Power (%)


Power vs Resistivity
(Molybdenum on DC1; Tooling Factor 16.4%;
Bulk Resistivity 5.3 µΩ-cm)
Power (%)
0
10
20
30
40
50
60
0.00E+00
1.00E-03
2.00E-03
3.00E-03
4.00E-03
5.00E-03
6.00E-03
7.00E-03
Resistivity (Ω-cm)

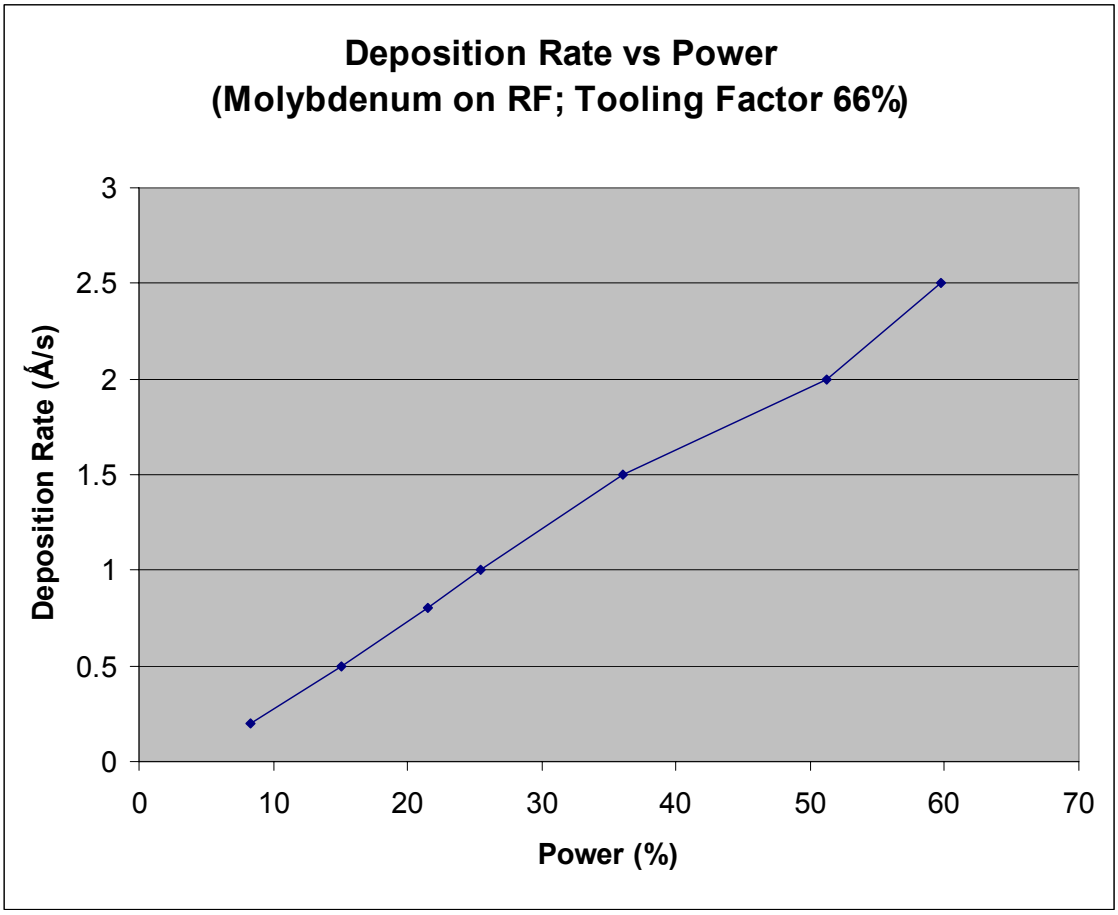
This data shows a roughly linear relationship between deposition rate and power for the sputtering of molybdenum. The power vs. resistivity graph also shows decreasing value of resistivity for higher powers of sputtering. The problem with sputtering at higher powers is that past 80% power, the sputterer fails to strike the plasma, ending the sputtering of molybdenum. Therefore, sputtering at high powers are limited to powers less than 80%. Even at the highest power, the resistivity of the molybdenum is two orders of magnitude too high (compared to the bulk resistivity).

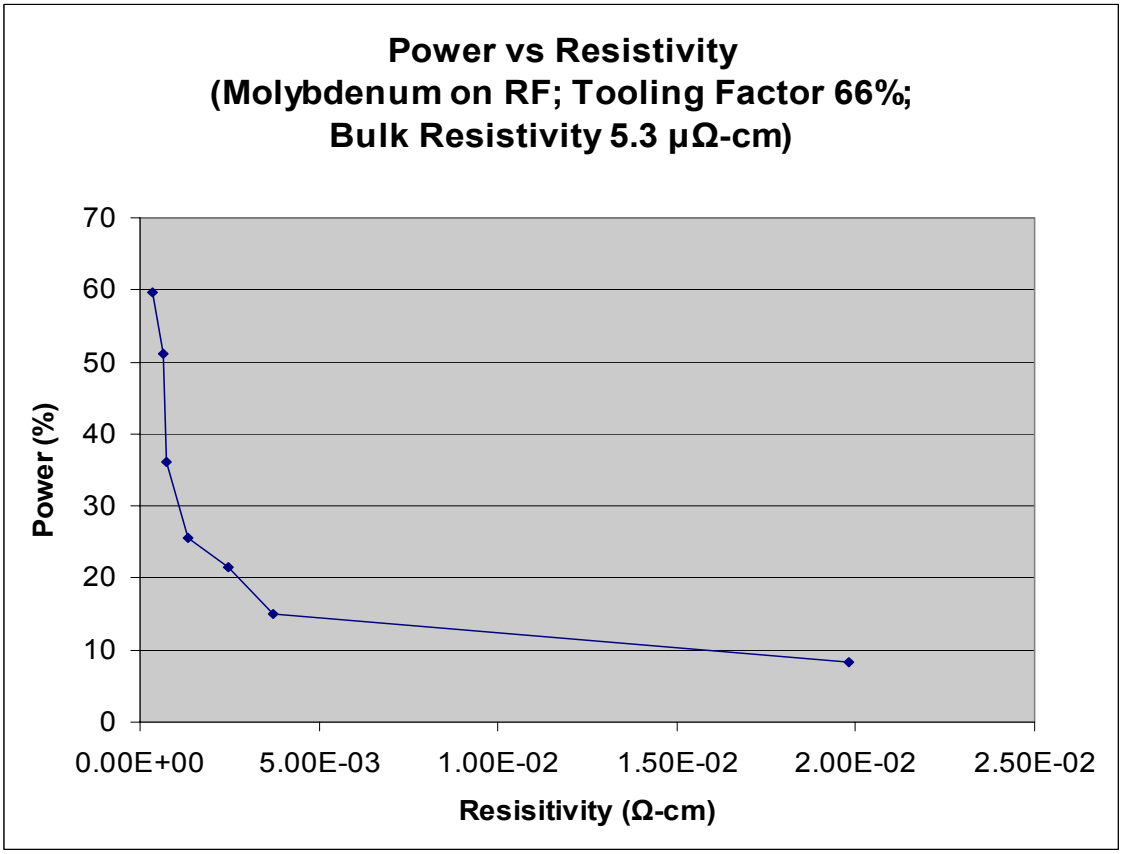
The next batch of data involves changing the molybdenum target from the DC1 source to RF source. Similar experimentation procedures are followed (as with testing on the DC1). The following data is obtained from the RF sputtering:

**Molybdenum on RF; Tooling Factor: 66.0 %; Bulk Resistivity: 5.3 x $10^{-6}$ Ω-cm; Molybdenum Melting Point: 2896 K, Molybdenum film thickness ~1000 Å, Sputtering Pressure: 10 mTorr**

| | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 |
|---|---|---|---|---|---|
| Power (%) | 51.18 | 8.27 | 15.05 | 25.47 | 59.69 |
| Dep. Rate (Å/sec) | 2 | 0.2 | 0.5 | 1 | 2.5 |
| Four Point Probe Resistivity (Ω-cm) | $6.52 \times 10^{-4}$ | $1.98 \times 10^{-2}$ | $3.72 \times 10^{-3}$ | $1.34 \times 10^{-3}$ | $3.45 \times 10^{-4}$ |

| | Sample 6 | Sample 7 |
|---|---|---|
| Power (%) | 21.49 | 36.04 |
| Dep. Rate (Å/sec) | 0.8 | 1.5 |
| Four Point Probe Resistivity (Ω-cm) | $2.45 \times 10^{-3}$ | $7.23 \times 10^{-4}$ |


Deposition Rate vs Power
(Molybdenum on RF; Tooling Factor 66%)
Deposition Rate (Å/s)
3
2.5
2
1.5
1
0.5
0
0
10
20
30
40
50
60
70
Power (%)


Power vs Resistivity
(Molybdenum on RF; Tooling Factor 66%;
Bulk Resistivity 5.3 µΩ-cm)
Power (%)
70
60
50
40
30
20
10
0
0.00E+00
5.00E-03
1.00E-02
1.50E-02
2.00E-02
2.50E-02
Resisitivity (Ω-cm)

The general trend observed by the RF and DC1 characteristics is that lower resistivities are found at high powers of sputtering. However, the RF gives slightly better resistivities at similar deposition rates. The resistivity using RF is still two orders of magnitude too high (compared to bulk resistivity).

Temperature and pressure could not be tested thoroughly. Sputtering at lower pressures gives more desirable resistivities, as evidenced from several measurements performed. (Different substrate indices were tested, but several did not sputter. Those substrate indices were 6, 7, 8, 10, and 14). The data is as follows:

**Resistivity on RF source; Deposition Rate: 3 Å/s; ~75% Power**

| Substrate Index | 10 mTorr | 15 mTorr |
|---|---|---|
| 9 | -- | $4.24 \times 10^{-4}$ Ω-cm |
| 11 | $2.41 \times 10^{-4}$ Ω-cm | -- |
| 12 | -- | $5.39 \times 10^{-4}$ Ω-cm |
| 13 | $1.82 \times 10^{-4}$ Ω-cm | -- |
| 15 | $1.77 \times 10^{-4}$ Ω-cm | -- |

Temperature and pressure settings could not be changed significantly on the sputterer. The pressure could be adjusted between 10 mTorr and 15 mTorr by changing the substrate index in the sputtering recipe. However, lower pressures (<10 mTorr) could not be obtained. In addition, an attempt to use the temperature gauge on the sputterer to heat the substrate failed. This was tried because lower resistivities could be reached by heating the substrate to approximately 1/3 the melting point of the molybdenum target. Unfortunately, this setting did not work and could not reach 1/3 the melting point of molybdenum as required.

**Conclusion:**

Low resistivity is obtained when sputtering is performed at low pressures, high power, and high deposition rates. Low pressure and high power are crucial variables in the development of low resistivity molybdenum film. Low pressure sputtering allows for a long mean free path and large concentrations of molybdenum to grow on the substrate, and sputtering at high powers results in a densely-packed grown film. Both conditions allow for low resistivity films.

**Acknowledgements:**

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