CHAPTER 5

STABILITY OF GOLD COATED FIELD EMITTER ARRAYS

5.1. Introduction

For a good field emission material, apart from having a low work function, it should be mechanically stable, easy to fabricate and should not be oxidized easily. Enhancements in field emission from Si tips, covered by super thin diamond-like carbon films were investigated by Litovchenko et. al.,\(^1\) who also studied the effect of different types of coatings and surface treatments (electrochemical etching, H\(^+\) implantation, and Cs enriched layers) on the electron field emission from Si tips. Coatings of Cu-Li alloy films on gated Si tips, resulted in a very low emission voltage.\(^2\)

Several Ir field emitter arrays were fabricated by Chalamala et. al, who reported that in spite of a slightly lower aspect ratio compared to Mo, in the presence of O\(_2\), Ir FEAs showed improved current stability to their Mo counterparts.\(^3\) The pressure dependency of emission currents of Si, Mo, Au and SiC field emitters were investigated and also showed improved emission current stability.\(^4\)

The effect of in situ carbon coatings on spindt type Mo tips was investigated by Mousa et. al, who reported an increase in stability of field emission current after the coating process.\(^5\) The emission stability of Mo FEAs coated with diamond-like carbon films, was investigated.\(^6\) Field emission from diamond coated field emitters yielded significant increase in emission current and lowered the F-N slopes.\(^7\) By applying a thin layer of Cesium on FEAs, there was a significant reduction in operating voltage.\(^8\) Similar effects were observed by depositing K and Li on Spindt type microcathode arrays.\(^9\)
Electron emission enhancement by coating Spindt type field emitter array cathodes with several monolayers of Ti, Zr and Hf has also been reported.\textsuperscript{10} Nitrides of transition metals like Nb, Zr and Ti were fabricated and tested for emission current stability.\textsuperscript{11} Coating Mo FEAs with thin ZrC films resulted in almost a ten-fold increase in the emission current level.\textsuperscript{12}

In this chapter, we present the results of the experimental measurements on the interaction of O\textsubscript{2} with Au coated Mo FEAs. The stability of the FEA to O\textsubscript{2} exposure was found by measuring the emission and device recovery characteristics as a function of total O\textsubscript{2} exposure. The device lifetime resulting from O\textsubscript{2} exposures for longer periods of time is determined and the results are discussed.

Au does not oxidize easily and thus the change in work function due to O\textsubscript{2} exposure should be very small. Emission current degradation is sensitive to the fraction of the area of the uncoated FEA (Mo). The O\textsubscript{2} degradation tests have been carried out for different initial gate voltages, anode currents and duty cycles. The uniqueness of this kind of lifetime testing is that the Au coated half of the array and the uncoated half are subjected to identical conditions of O\textsubscript{2} exposure.

5.2. Au Coated Field Emitter Arrays - Experimental

Experiments were performed with six Au coated Spindt-type field emitter arrays. The arrays were manufactured by Pixtech for Texas Instruments. Of these, two FEAs were coated with Au on one half of the emission area, while the other half was uncoated. The first FEA was coated with 29Å of Au on one half of the emission area, while the other half was uncoated. All experiments were done in the pulsed mode for different duty cycles (0.5%, 1% and 5%) and the anode voltage was set to 320 V.
Most experiments were carried out in pulsed mode at 0.5% duty cycle, with an ON time of 50?s and an OFF time of 9.950ms. Using a dual 300MHz oscilloscope, we were able to measure the voltage drop across a 330? Resistor connected to the circuit. Dividing the voltage drop by the resistance we were able to calculate the anode current for the Au coated and the uncoated half. The delay between measuring the emission current from the uncoated and the Au coated side when ON, was 5ms.

A second FEA was coated with 25Å of Au on one half of the emission area, while the other half was uncoated. Similar experiments were performed on this array, but the measurements were only made for the Au coated half. The last four arrays were coated with 22Å, 45Å, 66Å & 90Å Au respectively. Using accelerated tests at 5% duty cycle, the long-term stability to O₂ exposures was measured. For anode current recovery, the duty cycle was increased to 25% without changing the gate voltage.

5.3 Emission Characteristics

5.3.1 Current-Voltage & Fowler-Nordheim Data

The array was activated at 3mA for two days before any tests were carried out. The I-V plot (Figure 5.1) is shown along with the Fowler-Nordheim plot of the 29Å Au coated half of the FEA along with the uncoated half (Figure 5.2). It was observed that the emission area of the Au coated half was much less than that for the uncoated half.

This strongly indicated that only a small fraction of the Au coated tips were actually emitting. Also, the anode current from the Au coated half for the same gate voltage, was almost an order of magnitude less than that for the uncoated (Mo) half. This was mainly due to the higher work function of Au.
Figure 5.1 I-V curves, for the Au coated half and the uncoated Mo half.

Figure 5.2 F-N plots, for the Au coated half and the uncoated Mo half.
Applying the Fowler-Nordheim equation, we can estimate the ratio of the emission areas of the uncoated side to that of the coated side. Using the work function values of Au and Mo, and from the slope of the F-N plot, the change in the field enhancement factor (tip geometry) after Au deposition, was calculated.

From the FN plots in Figure 5.2, the slopes for the Au coated half and uncoated (Mo) half are seen to scale with their work function. Using the values of the work function for Au and Mo, and from the FN slopes we can determine the ratio of the field enhancement factor \( b_{Au} / b_{Mo} \) before and after the Au deposition, using equation (5.1):

\[
( b_{Au} / b_{Mo} ) = ( \phi_{Au} / \phi_{Mo} )^{-3/2} \left( \frac{m_{Au}}{m_{Mo}} \right)
\]  

(5.1)

where, \( \phi_{Au} \) and \( \phi_{Mo} \) are the work functions of Au and Mo, and \( m_{Au} \) and \( m_{Mo} \) are the FN slopes for the Au coated half and uncoated half (Mo).

Using the work function values for Au and Mo and from the above slopes, we get

\[
( b_{Au} / b_{Mo} ) = 0.83
\]  

(5.2)

and the ratio of emission areas \( A_{Au} / A_{Mo} \) = 0.14 which indicates that only a fraction of tips are emitting from the Au coated half.
5.3.2 Degradation as a function of the Gate Voltage

The O$_2$ degradation experiments were done for 2 gate voltages i.e. 65V and 70V for a dose on 20000L. The initial anode currents from the Au coated half and uncoated half, were different for the same gate voltage. The current versus dose plot for 65V and 70V, are shown in Figure 5.3.

![I-t plots for Mo & Au at different Gate Voltages](image)

Figure 5.3 I-t degradation for different gate voltages, for the Au coated half and the uncoated Mo half.

The normalized current versus dose plots, are shown in Figure 5.4. For the uncoated side, increasing the gate voltage increases the extent of degradation but for the Au coated side the change was not so significant.
5.3.3 Degradation as a function of the initial Anode Current

The O₂ degradation experiments were done for 5 different anode currents i.e. 15mA, 28mA, 35mA, 41mA & 53mA as shown in Figure 5.5. The gate voltage for the Au coated half was approximately 15 – 20V higher than that for the uncoated (Mo) half in order to have the same current on the Au coated and uncoated (Mo) half.

At first the array was tested for stability i.e. the anode current should have less...
than 5% change after running for 5000s. The system had a base pressure of $2 \times 10^{-8}$ torr before $O_2$ was introduced. Then $1 \times 10^{-6}$ torr $O_2$ was gradually introduced into the chamber through a leak valve. Each of the above experiments ran for over 6 hrs.

Figure 5.5 $I_N$-t degradation for different anode currents, for the Au coated half and the uncoated Mo half.

5.3.4 Recovery of Anode Current

When the degradation was complete, the $O_2$ in the chamber was pumped out and the duty cycle was increased to 25%. The anode current was allowed to recover for a few hours until it attained its starting value. For the Au coated side, the recovery was quick
(15min) and the final current exceeded its initial value. This indicates that there may have been some MoO$_2$ on the FEA tips before they were coated with Au. After each degradation experiment, the FEA was cleaned by increasing the duty cycle. The process of oxide removal, was indicated by a reduction in the work function.

After emission current recovery, the gate voltage was further increased. The duty cycle was then changed to 0.5% and the system was allowed to run for several hours until the anode current was stabilized (less than 0.5% change in emission current). The results of the emission current recovery are shown in Figure 5.6 below.

![Figure 5.6 I$_N$-t recovery plots for Mo & Au at different Anode Currents](image)

Figure 5.6 I$_N$-t recovery plots for different anode currents, for the Au coated half and the uncoated Mo half.
5.3.5 Degradation as a function of the Au thickness

The accelerated tests at 5% duty cycle were performed for a long period of time (200,000s). The overall dose was 100 times larger than the earlier 20000s degradation tests. For this set of experiments, the arrays were completely coated with Au films of thicknesses of 22 Å, 45 Å, 66 Å and 90Å. An uncoated array was used as the control sample. The initial anode current for each of the above arrays was approximately 53mA, after activating each array for 2 days and stabilizing for 20,000s. The summary of the degradation versus Au thickness is shown in Figure 5.7.

![Figure 5.7 IN-t degradation experiments for Au coated FEAs (long term stability at 5% duty cycle for 200000s)](image)

Figure 5.7 IN-t degradation experiments for Au coated FEAs (long term stability at 5% duty cycle for 200000s)
5.4. Results and Discussion

For the arrays coated with 29 Å and 25 Å Au on half their area, for the same applied gate voltage, we would get a much lower value of emission current from the Au coated side than from the uncoated side. This was mainly because of the higher work function of Au (5.5eV) as compared to Mo (4.6eV).

Also, not all the tips were emitting from the Au coated portion, which was indicated by a much lower area, compared to the uncoated portion. From the experimental data for the degradation at different anode currents for the above FEA, the Au coated side was seen to degrade much less (33%) than the uncoated side (90%) after 20000 L of O₂ exposure. Ideally, we would not expect any degradation in emission current from the Au coated half.

One reason for this degradation may be that not all the tips that are emitting, are coated with Au and there may be a small fraction of uncoated tips. The following is a method of estimating the fraction of Mo emitter tips in the Au coated half of the array.

The assumptions are that the anode current from the Au coated side does not change due to the Au coated tip degradation, the fraction of Mo remains the same throughout the experiment along with the tip geometry, as we recover the entire initial anode current.

Let \( f \) be the fraction of Mo tips and \( I'_{Au} \) be the current from only the Au coated tips.

**For a 65V Gate Voltage,**

Before Degradation: \( I_{Mo} = 26.52\text{mA}, I_{Au} = 2.16\text{mA} \)

After Degradation: \( I_{Mo} = 8.56\text{mA}, I_{Au} = 1.37\text{mA} \)

Thus the 2 equations, we have are:
\[ 2.16 = I'_{\text{Au}} \times (1 - f) + 26.52 \times (f) \quad (5.3) \]
\[ 1.37 = I'_{\text{Au}} \times (1 - f) + 8.56 \times (f) \quad (5.4) \]

Solving the above equations, we get \( f = 0.044 \) or \( 4.4\% \) uncoated Mo tips on the Au coated side.

**For a 70V Gate Voltage,**

Before Degradation: \( I_{\text{Mo}} = 42.94\text{mA}, I_{\text{Au}} = 4.00\text{mA} \)

After Degradation: \( I_{\text{Mo}} = 9.28\text{mA}, I_{\text{Au}} = 2.30\text{mA} \)

Thus the 2 equations, we have are:
\[ 4.00 = I'_{\text{Au}} \times (1 - f) + 42.94 \times (f) \quad (5.5) \]
\[ 2.30 = I'_{\text{Au}} \times (1 - f) + 9.28 \times (f) \quad (5.6) \]

Solving the above equations, we get \( f = 0.05 \) or \( 5.0\% \) uncoated Mo tips on the Au coated side.

From the above results, we see that, there is only a slight change in the fraction of uncoated tips. Also there is some sputtering of the Au coated tips and the fraction of uncoated Mo tips would thus increase as we do more degradation experiments. A 5% fraction of uncoated Mo tips in the Au coated half causes a significant degradation (33%) in emission current. The stability of the Au coated arrays is thus sensitive to the fraction of uncoated Mo tips. For a given Gate Voltage, we have the following:

\[ D_{\text{Au}} = D_{\text{Mo}} \times f \times \left( \frac{I_{\text{Mo}}}{I_{\text{Au}}} \right) \quad (5.7) \]

Where,

\( D_{\text{Mo}} = \% \text{ degradation of the uncoated (Mo) portion} \)

\( D_{\text{Au}} = \text{Apparent \% degradation of the Au coated portion} \)

\( f = \text{Fraction of Mo in the Au coated portion} \)
\[ I_{Mo} = \text{Anode current from the uncoated (Mo) portion} \]

\[ I_{Au} = \text{Anode current from the Au coated portion} \]

The above equation works well for an Au coated array with a very small fraction of Mo (Since \( I_{Au} \approx I'_{Au} \)).

The long-term stability tests were done for 4 Au coated arrays of thickness 22 Å, 45 Å, 66 Å and 90Å. The results showed more or less the same amount of degradation for the Au coated FEAs and the uncoated FEA. The main reason for this was that the FEAs may have not been coated with Au completely and this was strongly indicated from their I-V data shown in Figure 5.8 and F-N data shown in Figure 5.9.

![I-V Plots for different Au coated FEAs](image)

Figure 5.8 I-V curves for 2 Au coated FEAs and an uncoated FEA showing similar emission characteristics.
Figure 5.9 F-N plots for 2 Au coated FEAs and an uncoated FEA indicating similar emission characteristics.

For the FEAs coated with Au only on one half of their area, for a given emission current, the Au coated half needed a higher gate voltage (10-15V) than the uncoated half, i.e. the emission current scaled with the work function. This was not the case for the 4 Au coated samples as the initial gate voltage required to get the same anode current from each of them was similar to that from the uncoated array, which shows that the fraction of Au coated tips must be less.

The following is a method of estimating the fraction of the FEA area actually coated with Au ($f$). The assumptions are that the anode current from the Au coated
emitter tips, does not change due to the degradation. Also, the fraction of Mo remains the same throughout the experiment along with the tip geometry.

For the uncoated, 22Å Au coated and 44Å Au coated FEAs, we have different values of the initial gate voltage required to obtain 53mA, which are shown below:

\[ V_g = 69.6 \text{ V (uncoated FEA)} \]
\[ V_g = 73.7 \text{ V (FEA coated with 22Å Au)} \]
\[ V_g = 70.5 \text{ V (FEA coated with 44Å Au)} \]

Also, the value of degraded emission current for each of the above FEAs, after 100,000s (or 80,000L of O\(_2\)) is shown below:

\[ I_a = 9.96\text{mA (uncoated FEA)} \]
\[ I_a = 19.24\text{mA (FEA coated with 22Å Au)} \]
\[ I_a = 13.32\text{mA (FEA coated with 44Å Au)} \]

**For the 22 Å Au coated FEA,**

\[ V_g = 73.7 \text{ V} \]

We can estimate the emission current from the uncoated area of the above FEA using the uncoated FEA I-V data. We substitute the value of \( V_g = 73.7 \) in the equation below:

\[ \ln ( I_a / V_g^2 ) = (-484.48 / V_g) \]  \( \text{(5.8)} \)

Solving the above equation yields, \( I_{Mo} = 88\text{mA} \) if the array were uncoated.

Now we have 2 equations to solve which are,

\[ 53 = 88 \times (1-f) + I_{Au} \times (f) \]
\[ 19.24 = 9.96 \times (1-f) + I_{Au} \times (f) \]

where \( I_{Au} \) is the emission current from the Au coated Tips.

Solving the above equations, we get \( f = 0.57 \) or 57% Au coated tips.
For the 44 Å Au coated FEA,

\[ V_g = 70.5 \text{ V} \]

We can estimate the emission current from the uncoated area of the above FEA using the uncoated FEA I-V data. We substitute the value of \( V_g = 70.5 \) in the equation below:

\[
\ln \left( \frac{I_a}{V_g^2} \right) = \frac{-484.48}{V_g} \quad (5.11)
\]

Solving the above equation yields, \( I_{Mo} = 60 \text{mA} \) from the uncoated area of the FEA.

Now we have 2 equations to solve which are,

\[
53 = 60 \times (1 - f) + I_{Au} \times (f) \quad (5.12)
\]

\[
13.32 = 9.96 \times (1 - f) + I_{Au} \times (f) \quad (5.13)
\]

where \( I_{Au} \) is the emission current from the Au coated Tips.

Solving the above equations, we get \( f = 0.21 \) or 21% Au coated tips.

The above results indicate that the emission current from the FEA having a higher fraction of Au coated tips (22Å Au) degraded to a lesser extent than that with a lower fraction (44Å Au). One reason for this discrepancy is that the thickness of the Au coating on the FEA may have been much less than 44Å, as it was not experimentally determined using RBS.
REFERENCES