Influence of process variables on electron beam chemical vapor deposition of platinum

D. Beaulieu
George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, 813 Ferst Drive, Atlanta, Georgia 30332

Yong Ding and Z. L. Wang
School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332

W. J. Lackey[a)]
George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, 813 Ferst Drive, Atlanta, Georgia 30332

(Received 22 April 2005; accepted 8 August 2005; published 22 September 2005)

Electron beam chemical vapor deposition was performed in a modified environmental scanning electron microscope to deposit platinum structures. Process variables including voltage, beam current, deposition time, dwell time, and line time were studied in statistically designed and analyzed experiments on fiber (pillar-like structures) and line (wall-like structures) deposition. Deposition rates and geometric features such as aspect ratio were optimized. Results from the experimentation showed the importance of the beam current, voltage, and adsorbate replenishment to the deposition process. Growth rates up to 0.9 μm/min were obtained for short deposition times. © *2005 American Vacuum Society.* [DOI: 10.1116/1.2050672]

I. INTRODUCTION

Electron beam chemical vapor deposition (EBCVD) is a technology that uses an electron beam to provide localized deposition for fabrication of nanoscale structures or devices. In EBCVD, primary electrons from the beam impact a substrate, causing secondary electrons to be emitted. These secondary electrons play a prominent role in dissociating adsorbed reagent molecules to form a deposit on the substrate and volatiles that are evacuated from the chamber. The deposition process depends on many factors including the precursor properties and the electron beam properties. If the electron beam is not moved relative to the substrate, a dot is grown. A fiber is grown if the growth time is increased. If the beam is moved, lines or other structures can be deposited as in rapid prototyping. High aspect ratio structures can be deposited, an example of which are fibers deposited on atomic force microscope tips to improve resolution.[1] Alternative names for the process are electron beam induced deposition (EBID) and focused electron beam induced deposition (FEBID).

Direct fabrication technologies such as laser CVD[2] have resolutions on the order of 10–100 μm, which is approximately ten times the wavelength of the laser. A focused ion beam (FIB)[3,4] can also be used as a direct fabrication technology, with deposition occurring via ion beam decomposition of adsorbed precursor molecules. Typical resolutions for FIB are on the order of 100 nm. FIB technology has been used for device modification and mask repair. Inherent problems associated with FIB technology include damage to the sample in the form of milling and ion implantation. EBCVD is capable of resolution as small as 20 nm for a 30 kV beam and 7 nm for a 200 kV beam, allowing fabrication of nanometer scale devices.

Platinum has been deposited using EBCVD previously by several groups, including Takai *et al.*,[5] Hübner *et al.*,[6] and Koops *et al.*[7] Deposition was performed using $C_5H_5Pt(CH_3)_3$ as a precursor. Typical platinum deposits contain 10%–20% Pt and over 70% carbon, along with small amounts of oxygen. Deposits consisted of Pt nanocrystals in an amorphous carbon matrix. Growth rates up to 9 μm/min[7] have been reported for fibers, but typical values reported elsewhere ranged from 0.5 to 2 μm/min for short deposition times. Volumetric deposition rates ranging from approximately 0.6 to 0.06 μm^3/min have also been reported.[5] Increasing voltage has been shown to decrease the deposition rate. Increasing the deposition time typically leads to a decrease in the deposition rates, but Hübner *et al.*[6] did not report this effect over a short deposition time range. Higher beam currents have been shown in general to be preferable for higher deposition rates,[8,9] with the notable exception of carbon.[10] A thorough investigation of the deposition parameters for platinum, such as the voltage, beam current, deposition time, and beam scan speed has not been previously reported.

II. EXPERIMENTAL APPARATUS

A modified environmental SEM manufactured by FEI was used to perform platinum deposition. A gas injection system (GIS) was added to the ESEM. The gas injection system consists of a 0.5 mm inner diameter needle that inserts and retracts pneumatically along with a heating system. The reagent gas is generated from a Pt containing chemical paste that is located in a crucible integrated into the base of the needle of the GIS. The heating system is a Micro-Infinity

[a)]Author to whom correspondence should be addressed; electronic mail: jack.lackey@me.gatech.edu

temperature controller that heats the Pt containing paste to 40 °C. The Pt compound is $(CH_3)_3Pt((C_5H_5)CH_3)$, with a melting point of 30 °C. The needle insertion point is set to 9.9 mm vertically from the point where the electron beam exits the final aperture from the column. When using the GIS, it is possible to stay in high vacuum mode, meaning the pressure in the chamber is still on the order of 10^{-6} Torr. The microscope features a tungsten filament, and the primary electron beam parameters are the voltage (values range from 0.2 to 30 kV) and the spot size (values are on an arbitrary scale from 1.0 to 8.0). The spot size encompasses both the physical diameter of the electron beam as well as the beam current, and both of these values increase exponentially with increasing spot size for the tungsten filament microscope.

III. EXPERIMENTAL PROCEDURE

Experiments for platinum deposition using the GIS were performed at a pressure on the order of 10^{-6} Torr. The experiments were performed using small pieces of a polished (100) *p*-type silicon wafer as substrates. Suitable deposition sites were chosen on the substrates, typically near an edge to allow for easier post-deposition imaging. The experiments were performed in a randomized fashion so as to minimize any bias.

Statistically designed and analyzed factorial and central composite experiments were performed for platinum fiber deposition, and the variables investigated were deposition time, voltage, and beam current. The factorial fiber experiments were a two-level, three factor design. The same variables were investigated for the fiber central composite with star points design. A smaller range of factor settings was used for the central composite design than for the factorial design, but the central composite design is more powerful for investigating interaction effects.

Factorial and central composite experiments were also performed to study platinum line deposition. The variables studied for these experiments were voltage, beam current, dwell time, and line time. Dwell time refers to the duration of time the beam spends on a single pixel, and line time refers to the amount of time required for the beam to return to a specific pixel when scanning. The first factorial line experiment performed was a two-level, three factor design with voltage, beam current, and dwell/line time as the variables. The dwell time and line time are proportional to each other (for the same resolution), so for this experiment it was not possible to separate out the effects of one from the other. The same variables were investigated using a central composite with star points design. Separate two-level, three factor experiments were also performed in order to separate out the effects of the line time and the dwell time. For these experiments, dwell time and line time were varied independently by varying the pixel resolution. The other factors studied were the voltage and the beam current. Ranges for the variables were dictated by the capabilities of the microscope and the constraints of the experimental design.

Upon completion of the experiments, samples were mounted on a 90° angle aluminum mount and SEM images

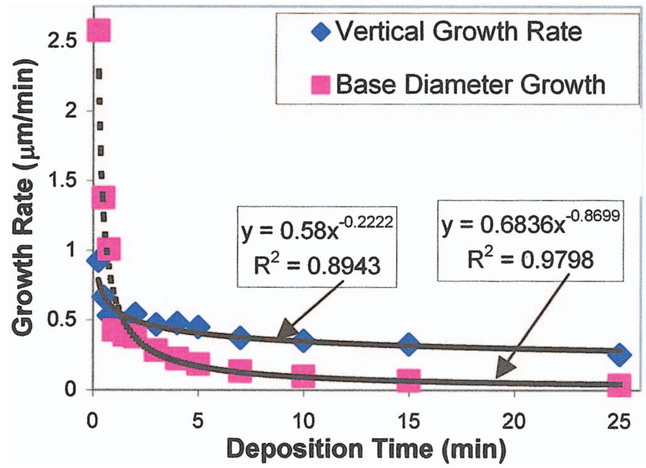

FIG. 1. Fiber growth rates versus deposition time.

were taken of the profiles of the fibers and lines. Measurements for fiber deposits were made for the diameter at the base and the height from base to tip. The parameters that were analyzed were the average vertical and base diameter growth rates. These rates were obtained by dividing the measured heights and diameters by the corresponding deposition time.

Measurements for line deposits for the height and width were taken at the midpoint of the deposits. This was done to provide a characteristic value for each line deposit and did not take into account buildup that occurred at the ends of the lines on some of the deposits. Measured parameters were then analyzed in STATGRAPHICS. Interaction terms were included for initial analysis of the response variables and some were subsequently excluded from the final analysis based upon their *p* values and effect on the correlation coefficient for the data and statistical model.

IV. EXPERIMENTAL RESULTS

Experimental results are presented in this section without discussion. Possible causes for observed effects are presented in Sec. V.

A. Preliminary experiments

Preliminary deposition experiments were performed to study the effects of increasing the deposition time for a constant voltage and beam current. The results for one of these experiments are summarized in Fig. 1, for which voltage and beam current were fixed at 30 kV and 5400 pA, respectively. As shown, the average fiber growth rates decrease significantly as deposition time increases, especially in the 0–5 min range. The effect is more pronounced for the base diameter, and it represents the fiber reaching a saturation diameter.

B. Platinum fiber deposition experiments

The variables investigated for each of the fiber deposition experiments were the voltage, beam current, and deposition

TABLE I. Settings and measurements for first fiber factorial experiment.

Trial	Voltage (kV)	Beam current (pA)	Deposition time (min)	Fiber height (μm)	Base diameter (μm)	VGR[a] (μm/min)	BDGR[b] (μm/min)
T1	10	5400	5	2.573	1.164	0.515	0.233
T2	30	50	5	1.374	0.783	0.275	0.157
T3	10	5400	15	4.245	1.368	0.283	0.091
T4	10	50	5	0.488	0.639	0.098	0.128
T5	30	5400	5	2.958	0.704	0.592	0.141
T6	30	50	15	3.099	0.423	0.207	0.028
T7	30	5400	15	4.673	0.710	0.312	0.047
T8	10	50	15	1.756	0.657	0.117	0.044

[a]VGR=vertical growth rate.
[b]BDGR=base diameter growth rate.

time. Fixed settings for each experiment included a working distance of 10.1 mm and a magnification of 8000×.

1. First platinum fiber factorial experiment

The settings used for the variables in the first two-level, three factor experiment for Pt fiber deposition were 10 and 30 kV for voltage, 100 and 5400 pA for beam current, and 5 and 15 min for deposition time. Table I summarizes the operating conditions and measurements made for this experiment. Data for other experiments are available.[11]

Analysis of the vertical growth rate results indicated the factors which had a statistically significant effect at the 95% confidence level were the beam current, deposition time, and the beam current-deposition time interaction term. The general trends indicated an increase in the vertical growth rate with increasing beam current, and a decrease with increasing deposition time. Figure 2 shows the response contours for a constant voltage. The correlation coefficient for this analysis was 97.3%. The four data points for 30 kV are included in Fig. 2. Note the excellent agreement between these points and the response contours predicted by the regression model. The model accurately correlates the growth rate with the process variables.

For the fiber base diameter growth rate, the deposition time was the only factor which had a statistically significant effect at the 95% confidence level. The general trends showed that an increase in deposition time leads to a drastic decrease in the fiber base diameter growth rate. The correlation coefficient for this analysis was 89.1%.

2. Second platinum fiber factorial experiment

Factor levels for the second two-level, three factor experiment were 5 and 30 kV for voltage and 1500 and 20 000 pA for beam current. The deposition time values investigated were the same as before, 5 and 15 min. All three of the factors were statistically significant at the 95% confidence level. The general trends indicated an increase in vertical growth rate with increasing beam current, and a decrease in vertical growth rate as voltage and deposition time are increased. Response contours for constant deposition time are shown in Fig. 3. The correlation coefficient was 94.4%.

Analysis of the fiber base diameter growth showed that deposition time and voltage were statistically significant factors at the 95% confidence level. The general trends show a decrease in base diameter growth rate as the voltage and deposition time increase. Response contours for constant beam current are shown in Fig. 4. The correlation coefficient was 94.7%.

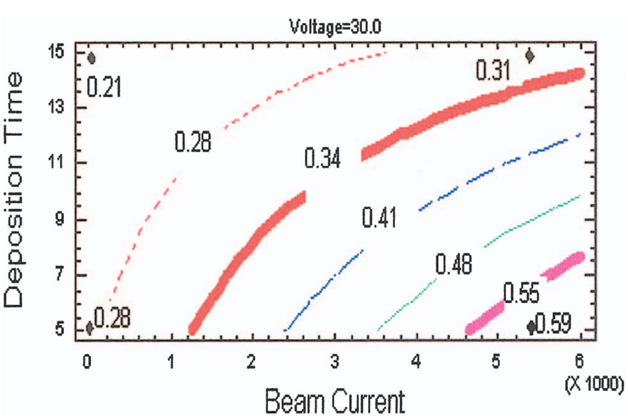

FIG. 2. Response contours for vertical growth rate (μm/min) for constant voltage from first Pt factorial fiber experiment.

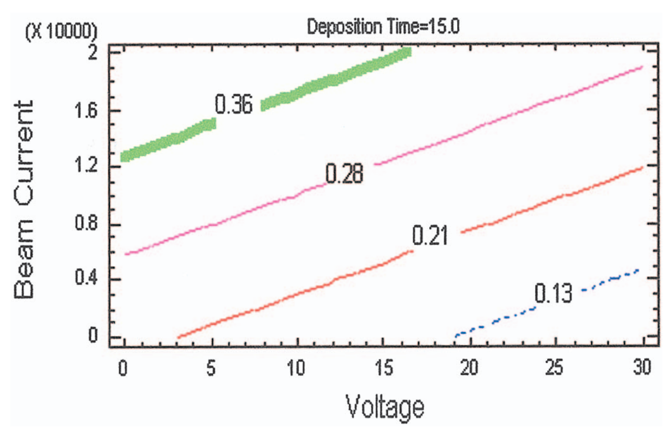

FIG. 3. Response contours for vertical growth rate (μm/min) for constant deposition time from second Pt factorial fiber experiment.

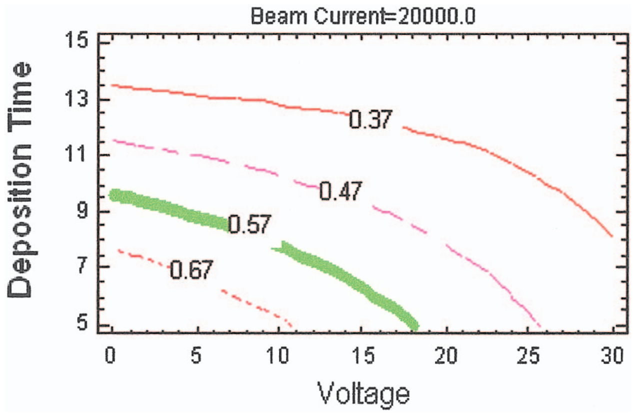

FIG. 4. Response contours for fiber base diameter growth rate (μm/min) for constant beam current from second Pt factorial fiber experiment.

3. Platinum fiber central composite experiment

Following the two-level factorial fiber trials, an experiment featuring a central composite with star points design was performed. In total, 16 fiber depositions were necessary for this experiment. Ranges for the variables were approximately 60–1500 pA for beam current, 5–30 kV for voltage, and 0.6–17.4 min for deposition time. All three of the variables were found to be significant at the 95% confidence level, along with the voltage squared term. Increasing voltage leads to lower vertical growth rates, as does increasing deposition time. Increasing beam current leads to higher vertical growth rates. Response contours for constant deposition time are shown in Fig. 5. Analysis of variance for the Pt fiber vertical growth rate indicated a correlation coefficient of 87.1%.

For the base diameter growth rate, the only terms found to be statistically significant at the 95% confidence level were the deposition time and deposition time squared term, which had a negative effect on the base diameter growth rate. Time was by far the dominant factor. ANOVA indicates a correlation coefficient of 70.6%.

C. Platinum line deposition experiments

The variables investigated for the line deposition experiments were voltage, beam current, and dwell/line time. Fixed settings for each experiment included a working distance of 10.1 mm and a magnification of 15 000×. The parameters analyzed were the average height/scan and the linewidth. The overall deposition time for each trial was held constant, but the line time was varied in these experiments. This means that a different number of scans of the beam are performed for a different value of the line time. To factor this discrepancy out, the measured line heights were divided by the corresponding number of scans performed. These height/scan values were multiplied by 10^6 to provide values that were capable of being properly analyzed in STATGRAPHICS, since initial attempts indicated software issues with the original magnitude of the height/scan numbers.

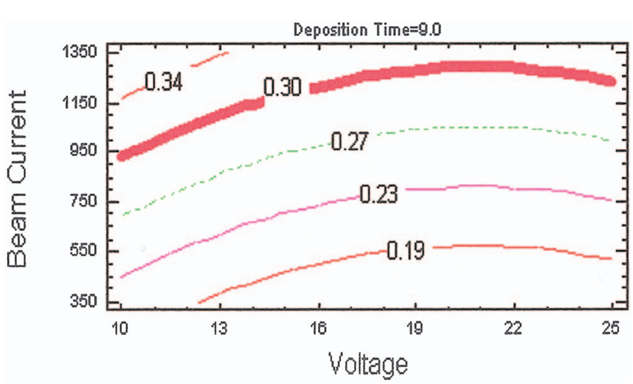

FIG. 5. Response contours for vertical fiber growth rate (μm/min) for constant deposition time from Pt central composite fiber experiment.

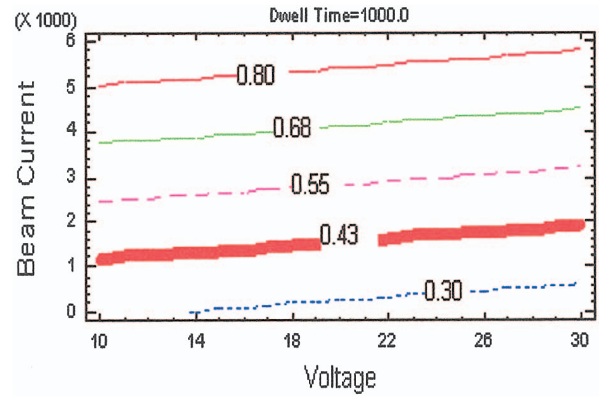

FIG. 6. Response contours for linewidth (μm) for constant dwell/line time from first Pt factorial line experiment.

1. First platinum factorial line deposition experiment

For the first two-level, three factor line deposition experiment, the variables and levels were voltage (10 and 30 kV), beam current (50 and 5400 pA), and dwell/line time (10 and 1000 μs dwell times, 10.60 and 1060 ms line times). A deposition time of 15 min was used.

Final analysis results for the height/scan showed a statistically significant increase with increasing beam current and dwell/line time. The correlation coefficient was 99.2%, indicating a very good fit between the data and the statistical model.

The linewidth trends differ from those for height/scan, with both the beam current and the voltage being statistically significant at the 95% confidence level. The general trends include a decrease in linewidth with increasing voltage, and an increase in linewidth for increasing beam current. Response contours for linewidth for constant dwell/line time are shown in Fig. 6. The correlation coefficient was 91.4%.

2. Central composite platinum line experiment

For the central composite with star points design, the variables were again voltage, beam current, and dwell/line time (with these factors varied simultaneously). Ranges for these variables were approximately 5–30 kV for voltage, 60–1500 pA for beam current, and 6–470 μs for dwell time (7–500 ms for line time). A deposition time of 20 min was used. Analysis for the height/scan indicated that the beam current,

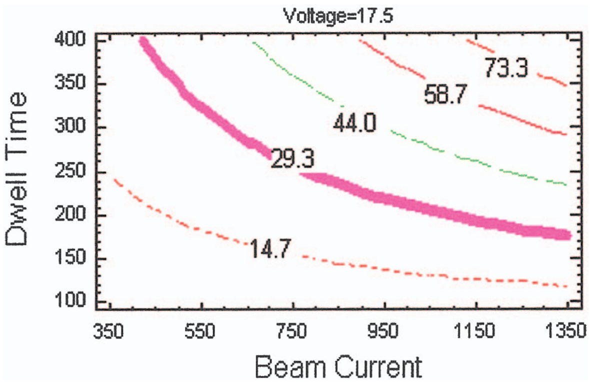

FIG. 7. Response contours for height/scan (μm/scan)$\times 10^6$ for constant coltage from Pt central composite line experiment.

dwell/line time, voltage, and the beam current-dwell/line time interaction terms were all statistically significant at the 95% confidence level. The general trends include a decreasing line height/scan with increasing voltage, and increasing height/scan for increasing beam current and dwell/line time. Response contours for the height/scan for constant voltage are shown in Fig. 7. The correlation coefficient was 84.6%.

For the linewidth, the results indicated that the dwell/line time, the dwell/line time squared, and the beam current-dwell/line time interaction terms had a statistically significant effect on the linewidth at the 95% confidence level. A general decrease in linewidth as voltage increases was observed. The correlation coefficient for this analysis was 74.2%.

3. Platinum factorial line time experiment

The effects of varying the line time were investigated as part of a two-level, three variable factorial experiment. The variables and levels were line time (0.55 and 2.08 ms), voltage (10 and 30 kV), and beam current (100 and 5400 pA). A deposition time of 20 min was used, along with a dwell time of 1 μs. The line time was the only variable found to be significant at the 95% confidence level for the final analysis. The correlation coefficient was 83.8%.

The linewidth trends differ from those for height/scan, with both the beam current and the voltage-beam current interaction terms being statistically significant at the 95% confidence level. The general trends showed a decrease in linewidth with increasing voltage, and an increase in linewidth for an increase in beam current. The correlation coefficient was 94.0%.

4. Platinum factorial dwell time experiment

A two-level, three factor experiment was performed to investigate the effects of varying the dwell time while holding the line time constant. The variables and levels were voltage (10 and 30 kV), beam current (100 and 5400 pA), and dwell time (0.25 and 1.0 ms). Fixed settings were a line time of 512 ms and a deposition time of 20 min.

Since the line time was held constant throughout this experiment, the same number of scans was performed for each deposition. The height/scan parameter was therefore not needed, and the line height was analyzed. Only the beam current was found to be statistically significant at the 95% confidence level. The correlation coefficient was 95.0%. The factor of interest, the dwell time, appears to have the least effect of all of the factors, with a P-value of 0.513.

The linewidth was also analyzed as a response variable, and the beam current was the only process variable to have a statistically significant effect at the 95% confidence level. An increase in beam current corresponded to an increase in linewidth. The correlation coefficient for this analysis was 92.3%. The dwell time was not shown to have a statistically significant effect on the linewidth, and it appeared to be the least influential factor, as it had the largest P value of all of the factors (0.492).

The regression coefficients generated from the statistical analyses for each of the line and fiber deposition experiments are summarized in the regression equations shown in Table II.

D. Optimization of platinum line and fiber deposition

STATGRAPHICS was used to predict process variable settings which should yield optimum results. Experiments were then conducted using these settings as guides. Optimization analyses were performed to maximize line and fiber aspect ratios, maximize fiber deposition rate (through maximizing both vertical and base diameter growth rates), and minimize linewidth. The central composite design fiber and line experiments were used for the optimization analyses for aspect ratio and linewidth, as they provided the most accurate illustration of the factor effects. The disadvantage of using the central composite experiments in this manner is that they covered a smaller range of values for the factors, especially the beam current. Analysis for fiber aspect ratio provided settings of 29 kV for voltage, 1378 pA for beam current, and 15.1 min for deposition time. The beam current suggested is near the higher end (1490 pA) of the values used for the original experiment. For comparison, more depositions were made with a higher beam current (5400 pA), but with the other settings identical. The settings suggested to maximize line aspect ratio were 30 kV, 1484 pA, and 177 μs dwell time (181 ms line time). The voltage and beam current suggested for optimization were near the upper limits for the analysis, so the beam current was increased to 5400 pA and more depositions were made. Optimization analysis for minimum linewidth suggested settings of 15.8 kV, 60.2 pA, and 423 μs dwell time (433 ms line time). Experiments were conducted at these settings, and the beam current was lowered (while keeping the other factors the same) and more lines were deposited at a beam current of approximately 20 pA, since the value recommended was the minimal value used for the central composite experiment.

The fiber deposition rate was also analyzed, and optimization analyses were performed on the two factorial fiber experiments. Results for both indicated settings of minimum voltage, maximum beam current, and minimum deposition

TABLE II. Regression equations generated from platinum deposition experiments.

Experiment	Parameter	Regression equation[a]
First fiber factorial	Vertical growth rate	$0.101-0.00465^{*}V+0.00009^{*}C-0.0022^{*}T-0.000004^{*}C^{*}T$
	Base diameter growth rate	$0.228-0.0015^{*}V+0.000007^{*}C-0.011^{*}T$
Second fiber factorial	Vertical growth rate	$0.368-0.0047^{*}V+0.000011^{*}C-0.0099^{*}T$
	Base diameter growth rate	$0.990-0.0198^{*}V+0.000004^{*}C-0.0524^{*}T+0.0013^{*}V^{*}T$
Fiber central composite	Vertical growth rate	$0.410-0.020^{*}V+0.0016^{*}C-0.0114^{*}T+0.0005^{*}V^{2}$
	Base diameter growth rate	$0.556-0.0011^{*}V+0.000017^{*}C-0.095^{*}T+0.0041^{*}T^{2}$
First line factorial	Height/scan $\times 10^{6}$	$19.12-0.98^{*}V+0.0002^{*}C+0.16^{*}D+0.00007^{*}C^{*}D$
	Linewidth	$0.573-0.012^{*}V+0.00008^{*}C+0.00005^{*}D$
Line central composite	Height/scan $\times 10^{6}$	$68.98-6.32^{*}V-0.0145^{*}C-0.001^{*}B+0.148^{*}V^{2}+0.00019^{*}C^{*}D$
	Linewidth	$1.045+0.0298^{*}V-0.00021^{*}C-0.00256^{*}D+0.00074^{*}V^{2}+0.0000031^{*}D^{2}$
Line time factorial	Height/scan $\times 10^{6}$	$-0.00855-0.0103^{*}V+0.000074^{*}C+0.366^{*}L$
	Linewidth	$0.538+0.0049^{*}V+0.000097^{*}C-0.0323^{*}L-0.0000033^{*}V^{*}C$
Dwell time factorial	Line height	$0.0381+0.0043^{*}V+0.000026^{*}C+0.1437^{*}D-0.0082^{*}V^{*}D$
	Linewidth	$0.3976-0.00717^{*}V+0.00003^{*}C-0.210^{*}D+0.00897^{*}V^{*}D$

[a] *V*=voltage (kV), *C*=beam current (pA), *T*=deposition time (min), *D*=dwell time (μs), *L*=line time (ms); Units: vertical, base diameter growth rate $=\mu$m/min; height/scan $\times 10^{6}=\mu$m/scan$\times 10^{6}$; linewidth $=\mu$m.

time (5 min). Depositions were thus performed at these settings, which had a larger minimum time value than the central composite experiment.

The results of the optimization experiments indicated that increasing the beam current leads to a considerable increase in the aspect ratio for both fibers and lines. The minimum linewidth obtained was approximately 200 nm for the two experiments performed at the suggested optimization settings, and less than 185 nm for the experiments performed at the lower beam current. It was impossible to obtain submicron features for high beam current values at 5 kV, since the beam diameter is greater than 1 μm for these settings. The smaller spot sizes obtainable with field emission microscopes would permit smaller diameter deposits.

E. Transmission electron miscroscope (TEM) analysis

Platinum fiber deposits were analyzed in a TEM, with energy dispersive spectroscopy, and electron energy-loss spectra used to determine the composition and structure. All deposits were found to be amorphous platinum, with no carbon detected. Figure 8 shows the typical deposit microstructure obtained. This is contrary to previously reported results, which noted upwards of 70% carbon content.[5,7,12,13] The reasons for this discrepancy are unknown at this time.

V. DISCUSSION OF RESULTS

The reagent used in our experiments was $(CH_3)_3Pt((C_5H_5)CH_3)$. The experimental results are compared to previous literature where a slightly different reagent, $C_5H_5Pt(CH_3)_3$, was used.

A. Variable effects

1. Voltage

For platinum fiber deposition, an increase in voltage leads to a decrease in vertical growth rate. The analysis for the central composite experiment (which covered the 5–30 kV range) indicated an effect of the square of the voltage as well

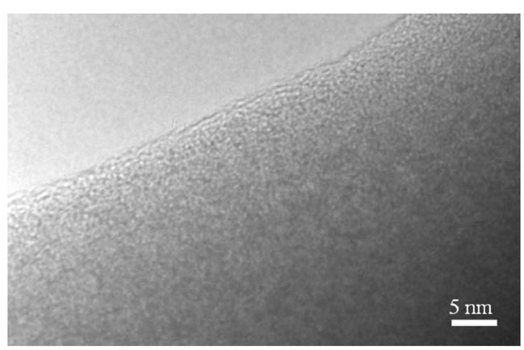

FIG. 8. Transmission electron microscope image of Pt deposit microstructure.

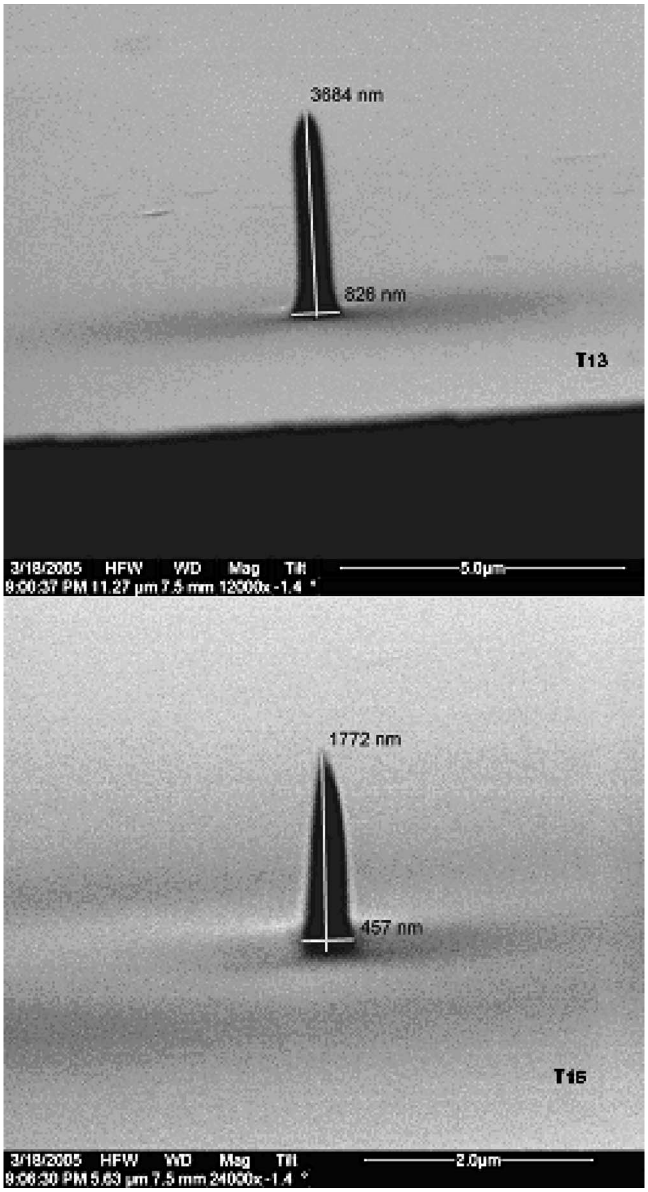

FIG. 9. Pt fibers deposited at 5 kV (top) and 30 kV (bottom) (fixed settings: 1,500 pA beam current, 15 min deposition time).

(both were statistically significant at the 95% confidence level). The base diameter growth rate appeared to exhibit a slight decrease as voltage was increased, but this was not statistically significant. Examples of the effect of voltage on fiber deposition are shown in Fig. 9. Similar effects were observed for platinum line deposition, as the height/scan and linewidth behaved in a consistent manner to vertical and base diameter growth rate. The observed decrease in linewidth with increasing voltage is a logical result, since the higher voltages also corresponded to smaller beam diameters for these experiments. It is also easier to manually focus the beam at higher voltages for the high magnifications that were used. The smaller linewidths at higher voltages would also correlate with lower secondary electron emission from the substrate.[5]

Takai *et al.*[5] reported volumetric deposition rates for platinum that decreased as voltage was increased from 1 to 30 kV. Virtually all of the decrease occurred in the 1–10 kV range. It was noted that this decrease appeared to mirror the decrease in secondary electron yield from (100) Si over this voltage range. These previously reported results agree with experimental data for this investigation, as the vertical growth rate showed a distinct decrease with increasing voltage, while there appeared to be minimal effects on the base diameter growth rate. Hübner *et al.*[6] reported that for small dot deposition the base diameter increased when the voltage was decreased from 15 to 2.5 kV.

2. Beam current

The beam current was a very important factor for fiber vertical deposition rate. An increase in beam current corresponds to an increase in the vertical growth rate, and this factor was statistically significant at the 95% confidence level in all experiments. The beam current has a much less significant effect on the fiber base diameter growth rate, and it was not found to be statistically significant in this case. For fixed voltage settings (30 kV), changing the beam current from 100 to 5400 pA leads to a vertical growth rate that is more than three times greater. Values for the average fiber vertical growth rates for this investigation ranged from approximately 0.07 to 0.55 μm/min. Examples of the effects of beam current on fiber deposition are shown in Fig. 10. The beam current had a similar effect on the height/scan for line deposition as it did for the vertical growth rate for fiber deposition. The platinum linewidth also appears to have a positive correlation with the beam current. This effect was considerably greater in the factorial experiments than in the central composite experiment, and these results are attributable to the fact that the higher beam currents used in these cases had considerably larger beam diameters.

Vertical growth rates for platinum fibers as high as 9 μm/min and in excess of 10^{12} nm/C at 20 kV have been reported.[7] Deposition rates can be limited by beam current or reagent gas flux.[14] The vertical growth rates obtained in this investigation ranged from 10^9 to 10^{11} nm/C.

3. Deposition time

The vertical growth rate for platinum fiber deposition decreased considerably as the deposition time increased. The initial average vertical growth rates (for 30 s deposition time) at 30 kV were approximately 0.3 and 0.9 μm/min for 100 and 5400 pA beam currents, respectively. For the same currents, as the deposition time was increased to 15 min, these rates dropped to approximately 0.06 and 0.3 μm/min, respectively. A constant fiber vertical growth rate over a short deposition time range (0.30–104 s) has been reported elsewhere.[6] This was not observed here, however. Better agreement is found with the results from Takai *et al.*,[5] who reported a vertical deposition rate of approximately 2 μm/min for a deposition time of 0.5 min. The effects of the deposition time on the vertical growth rate are

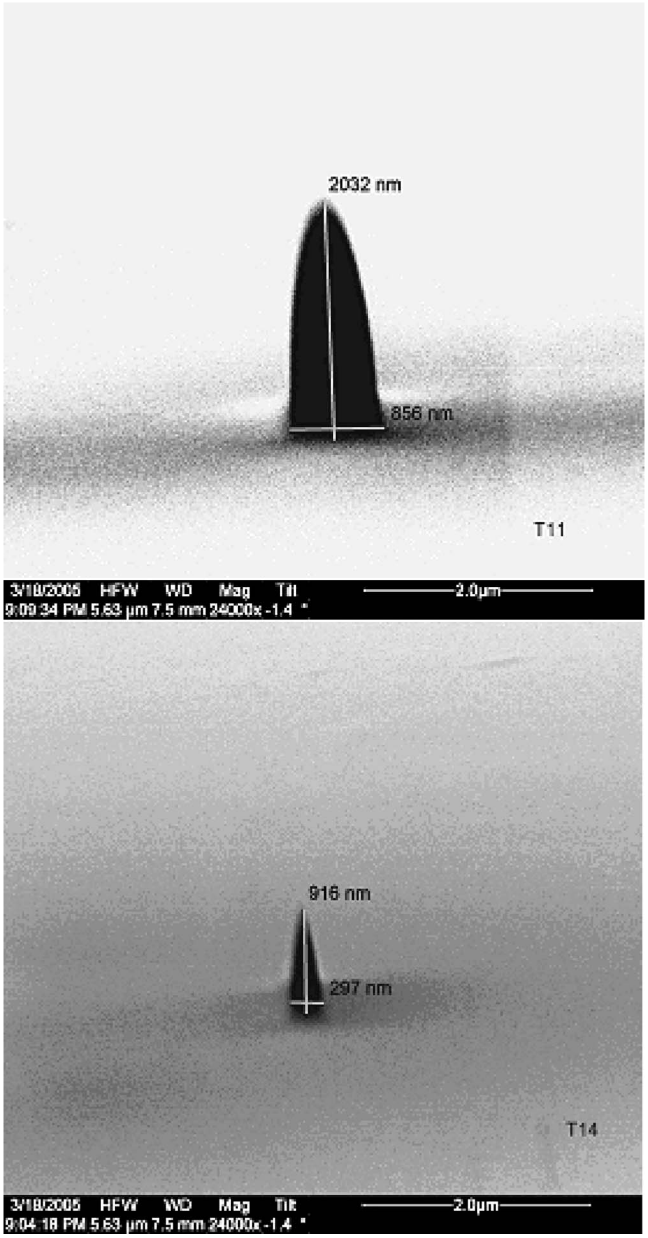

FIG. 10. Pt fibers deposited at 20,000 pA beam current (top) and 1,500 pA beam current (bottom) (fixed settings: 30 kV voltage, 5 min deposition time).

attributable to the decreased secondary electron input from the substrate and to the fact that reagent molecules must diffuse upward as the fiber continues growing.

The platinum fiber base diameter growth rate was dependent primarily upon the deposition time. The base diameter growth rate decreases sharply as the deposition time increases. This is expected as the fibers reach a saturation diameter as the deposition time increases. This maximum (or saturation) diameter is representative of the limiting range over which the secondary electrons can dissociate adsorbed molecules when the electron beam is held in a fixed position. The saturation effect concerning the maximum size (fiber diameter or linewidth) for a deposit is described by Schiffmann[10] and Silvis-Cividjian *et al.*[15] The diameter growth is essentially defined by the mean maximum electron path length inside the fiber, and Reimer[16] gives a general value for the inelastic mean free path for the secondary electrons in the 5–15 nm range.

4. Dwell/line time

Experiments were performed in which the dwell time was varied in conjunction with the line time, and these factors were also investigated individually. The results indicated that the combined effects of increasing both the dwell and line times was a significant increase in the height/scan. The dwell/line time term appeared to be the predominant factor in influencing the height/scan, and it was statistically significant at the 95% confidence level. The central composite platinum line experiment investigated a smaller range of values (from 6 to 470 μs for the dwell time and 6.6 and 500 ms for the line time), and it showed a definite decrease in linewidth as dwell/line time was increased. This factor was found to be statistically significant at the 95% confidence level for the central composite experiment.

The line time appeared to be the dominant factor in height/scan for platinum line deposition based on the factorial experiment that was performed for constant dwell time, and it was found to be significant at the 95% confidence level. Increasing the line time by a factor of 4 led to an almost fourfold increase in the height/scan values. When the dwell time was studied independently of the line time, experimental results did not show a statistically significant effect at the 95% confidence level for either the line height or the linewidth. This indicates that the effects of altering the dwell/line time simultaneously as described earlier are due primarily to the line time.

The dwell time and line time effects have been studied for W fiber deposition with a specialized system featuring an electrostatic beam blanker.[17] Holding the loop (i.e., line) time constant and increasing the dwell time led to a decreasing deposition yield due to progressing consumption of the adsorbate layer. Holding the dwell time constant and increasing the loop (line) time led to an increase in deposition yield to a saturation level due to a longer time for replenishment of the adsorbate layer. The combined dwell/line time effects studied here indicate that the adsorbate replenishment associated with the increasing line time is a more important factor than the adsorbate consumption resulting from increasing dwell time.

B. Platinum optimization results

Optimization analysis and experimentation indicated that the aspect ratio optimization for both line and fiber deposition indicated that high voltage (30 kV) and high beam current (5400 pA) were favorable for maximizing this parameter. For the minimum linewidth, medium voltage (15.8 kV) and low beam current (60 pA) were recommended, and results indicated that the low beam current, which corresponds to a smaller beam diameter, was a very important parameter. A long dwell time (420 μs) was also found to be preferable. The minimum linewidth obtained for a substantial deposition time (20 min) was under 200 nm. For the fiber deposition rates, low voltage (5 kV) and high beam current (20 000 pA) led to the maximum rates. For a tungsten filament microscope, such as the SEM used for this investigation, very high beam currents also correspond to substantially larger beam diameters, which means that it is difficult to achieve submicron features at the maximum deposition rates. Hübner *et al.*[6] reported that the platinum fiber diameter reached a saturation value of approximately 200 nm after a short deposition time. Optimal settings for a specific application would be determined by the feature size and process speed required for that application.

VI. CONCLUSIONS

Statistically designed and analyzed experimentation for platinum fiber and line deposition was performed. The effects of voltage, beam current, deposition time, dwell time, and line time were investigated. Results showed the importance of these parameters. Increasing beam current leads to an increase in deposition rates, while the opposite effect is observed for increasing voltage. Increasing the deposition time also leads to a decrease in the deposition rates. Increasing time for adsorbate replenishment appears to be an important factor as well.

[1] Y. Akama, E. Nishimura, A. Sakai, and H. Murakami, J. Vac. Sci. Technol. A **8**, 429 (1990).
[2] C. Duty, D. Jean, and W. J. Lackey, Int. Mater. Rev. **46**, 271 (2001).
[3] S. Matsui and Y. Ochiai, Nanotechnology **7**, 247 (1996).
[4] S. Reyntjens and R. Puers, J. Micromech. Microeng. **11**, 287 (2001).
[5] M. Takai, T. Kishimoto, H. Morimoto, Y. K. Park, S. Lipp, C. Lehrer, L. Frey, H. Ryssel, A. Hosono, and S. Kawabuchi, Microelectron. Eng. **41/42**, 453 (1998).
[6] U. Hübner, R. Plontke, M. Blume, A. Reinhardt, and H. W. P. Koops, Microelectron. Eng. **57–58**, 953 (2001).
[7] H. W. Koops, A. Kaya, and M. Weber, J. Vac. Sci. Technol. B **13**, 2400 (1995).
[8] I. Utke, T. Bret, D. Laub, P. Buffat, L. Scandella, and P. Hoffmann, Microelectron. Eng. **73–74**, 553 (2004).
[9] A. Perentes, A. Bachmann, M. Leutenegger, I. Utke, C. Sandu, and P. Hoffmann, Microelectron. Eng. **73–74**, 412 (2004).
[10] K. I. Schiffmann, Nanotechnology **4**, 163 (1993).
[11] D. Beaulieu, M. Eng. Thesis, G. W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA, 2005.
[12] H. W. Koops, C. Schössler, A. Kaya, and M. Weber, J. Vac. Sci. Technol. B **14**, 4105 (1996).
[13] L. Rotkina, J. F. Lin, and J. P. Bird, Appl. Phys. Lett. **83**, 4426 (2003).
[14] V. Scheuer, H. Koops, and T. Tschudi, Microelectron. Eng. **5**, 423 (1986).
[15] N. Silvis-Cividjian, C. W. Hagen, L. H. A. Leunissen, and P. Kruit, Microelectron. Eng. **61–62**, 693 (2002).
[16] L. Reimer, *Scanning Electron Microscopy*, 2nd ed. (Springer, Berlin, 1988).
[17] K. T. Kohlmann-von Platen, L. M. Buchmann, H. C. Petzoid, and W. H. Brunger, J. Vac. Sci. Technol. B **10**, 2690 (1992).