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Etch Trends in Electrochemical Machining with Ultrashort Voltage Pulses

Predictions from Theory and Simulation

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We present analytical and computational models used to investigate the dependence of etch resolution on pulse duration, tool radius, and etched feature aspect ratio in electrochemical machining with ultrashort voltage pulses. Our results predict that, for the high aspect ratio system in which the effect of trench top and bottom edges can be ignored, the increase of etch resolution with pulse length is a strong function of tool radius, while there is a significant dependence on etch depth for the low aspect ratio system in which the edge effects become important. A detailed analysis of the etch trends is presented.

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In recent years, various electrochemical systems have been investigated to modify substrates on the micrometer and nanometer length scales. One such system employs a tool electrode and voltage pulses of less than 100 ns to localize the electrochemical reactions, which allows precise etching of or deposition on the workpiece (substrate).[1] In electrochemical machining with ultrashort voltage pulses, a tool electrode is held in close proximity to an electrically active workpiece. The tool is then biased with an ultrashort voltage pulse, thus charging the electrochemical double layers at both the tool and workpiece. Due to the varying lengths of the current pathways from the tool to the workpiece through the electrolyte, regions of the double layer at the workpiece charge at different rates, analogous to a capacitor in a resistor-capacitor (RC) circuit charging more slowly if the resistance is increased. This results in a localized modification of the workpiece, as only the overpotential in the region near the tool grows large enough during the voltage pulse to allow etching. To date, this technique has been used with various workpiece materials, including copper,[1-3] gold,[1,2,4-6] stainless steel,[7,8] p-type silicon,[1,9] and nickel.[3,10] Recent experimental work on these systems has shown a direct relationship between etch resolution and pulse length.[10] At present, however, precise analysis of the etch trends is still lacking, despite its importance in guiding the rational design and fabrication of nanostructured materials and systems.

In this paper, we examine systematically the relationship between pulse duration and etch resolution for the first time using a combination of theory and computation. We first consider a two-dimensional high aspect ratio trench system in which the effect of top and bottom edges can be ignored. We find that as the pulse duration is increased, the resulting increase in the etch resolution must be less than linear for all pulse durations and tool radii typically employed in micro- and nanomachining. We also demonstrate that only the limiting case of one-dimensional behavior, seen in systems with a large ratio of tool radius to etch resolution, is characterized by a linear increase in etch resolution with pulse duration. In addition, we look at a low aspect ratio system in which the edge effect is important. We find that the etch resolution is a strong function of etch depth, varying from sublinear to superlinear with pulse duration. While such detailed analysis of etch resolution is unavailable experimentally, the overall trend in the relationship between pulse duration and etch resolution is consistent with experimental observations.

Model and Simulation

For the high aspect ratio system which exhibits purely two-dimensional behavior, we considered a system similar to one used to measure resolution experimentally,[10] as depicted in Fig. 1a. A cylindrical tool electrode first etches into the workpiece vertically, and then is moved laterally along the workpiece surface at a constant rate, forming a trench. If we consider a cross-sectional plane parallel to the workpiece surface and away from both the workpiece surface and bottom tip of the tool electrode, we isolate a region with fully two-dimensional characteristics. Here, the resolution is defined as $d_1 =$ (trench width-tool diameter)/2, with the trench width measured in the wake of the tool electrode once a steady-state trench width is achieved (Fig. 1b).

With the domain defined, the strategy of the computational model is as follows. First, circuit theory elements are used to describe the simulation components (tool, workpiece, electrolyte, and electrochemical double layers) and subsequently combined to find the evolution of the overpotential during the application of a voltage pulse at different regions of the workpiece interface. Next, the time and spatially variant overpotential information is used to obtain time-averaged spatially variant dissolution currents. Finally, these currents are converted to etch rates, which are in turn used to evolve the workpiece interface. This process is repeated until reaching a steady-state trench width downstream of the tool, whereupon the simulation is terminated and the resolution determined. We note that the effect of the etch product on electrolyte resistivity in the gap region between the tool and workpiece is not considered, as the low etch rates and micrometer length scale resolutions considered allow for diffusion of the product out of this region. Also not considered is redeposition of the product on the tool or workpiece, as experimental systems typically bias the tool against deposition during the pause period and the dissolution rate exceeds the redeposition rate significantly.[1]

To adapt the two-dimensional domain defined above for our computational model, a mesh was applied, with the electrolyte region modeled as a network of interconnected resistors, as shown in Fig. 1c. Connections to the tool and workpiece electrodes are made through capacitors in parallel, representing the electrochemical double layers. While this is not a realistic depiction of the behavior of the double layers at equilibrium, ignoring the polarization resistance has little effect on the transient charging behavior, assuming polarization resistances which are significantly larger than the electrolyte resistance. Reflective boundary conditions are used for unbounded electrolyte regions, with the simulation domain chosen to include all regions with significant etchrates (typically all regions within twice the expected etch resolution from the tool electrode).

The initial potential upon application of a voltage pulse was found by applying Kirchoff's Law to nodes within the electrolyte. The evolution of the potential within the electrolyte and overpotentials at the tool and workpiece were then calculated through further application of Kirchoff's Law in parallel with the charging of the double layer capacitors. After evolving the overpotential during the length of the pulse, Tafel behavior[11] was used at each workpiece capacitor to find the local dissolution current. Integration of this current over the pulse length followed by normalization by the combined pulse and pause periods then gave the local average etch rate.

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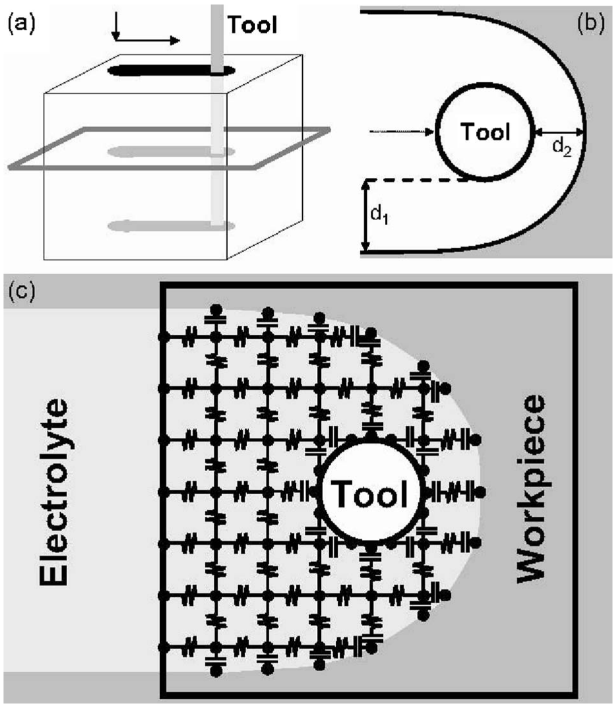

Figure 1. (a) Machining system used to measure resolution. Two-dimensional region used in computational model indicated by plane. (b) Definition of resolution (d_1) and gap space at the leading edge of the tool (d_2). (c) Simulation domain after application of mesh. Resistors connect nodes in the electrolyte. Electrochemical double layers represented by capacitors.

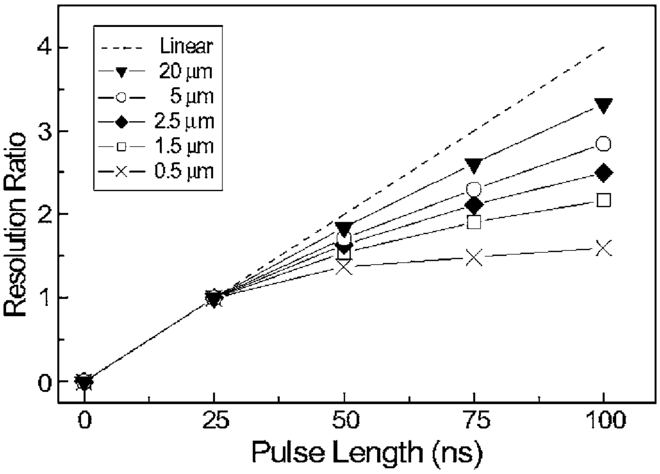

Figure 2. Etch resolution ratios relative to that of a 25 ns pulse duration for the indicated tool radii. Absolute resolutions for at the 25 ns pulse length are 1.14, 1.96, 2.26, 2.67, and 3.24 µm in order of increasing tool radius.

The level set method was used for interface tracking.[12] Details of the transient current behavior and feature profile evolution for this model are found elsewhere.[13,14]

Parameter values were typical of those used in experimental systems. A −2.3 V pulse was applied to a (nominally tungsten) tool moving laterally in a copper workpiece at 1.5 µm/min for durations ranging from 25 to 100 ns, with a pulse-to-pause ratio of 1:10. (The tool speed affects insignificantly the etch results unless varied by an order of magnitude.) An electrolyte with resistivity 27.71 Ω cm was used (corresponding to a 0.1 M copper sulfate/0.075 M sulfuric acid solution) in conjunction with constant capacities of 10 µF/cm^2 for both tool and workpiece.

Results and Discussion

Figure 2 shows the ratios of etch resolutions for different pulse lengths relative to that for a pulse length of 25 ns for tools with radii ranging from 0.5 to 20 µm. For all tool radii, the ratios are increasingly sublinear as the pulse length increases. As the tool radius is increased, the ratios move closer to linear behavior. Thus, in general terms, as the ratio of the absolute resolution to the tool radius decreases, the relationship between etch resolution and pulse duration becomes increasingly linear. For reference, the absolute resolutions for the 25 ns pulse duration range from 1.14 to 3.24 µm for tool radii of 0.5 and 20 µm, respectively.

This follows the trends that can be derived from a stationary two-dimensional system. Here we consider a fixed cylindrical tool located within a workpiece in a concentric arrangement, with electrolyte in the annular region. We define the resolution as the width of the annular region, $r_2 - r_1$, where r_2 is the radius at which the workpiece region begins and r_1 is the radius of the tool. For any such system, we can find the etch rate as above by first deriving the evolution of the overpotential at the workpiece surface, then integrating the resulting dissolution current and normalizing by the pulse-pause cycle length. For our model system, we consider an applied potential E with a pulse duration of length t. At any time, the applied potential is equal to the resistive potential of the electrolyte plus the overpotentials at the tool (η_1) and workpiece (η_2)

$$E = \frac{dq}{dt}R + \eta_1 + \eta_2 \qquad [1]$$

where q is charge and R is the electrolyte resistance. For a constant capacity c at both surfaces and electrolyte resistivity ρ, we can further substitute to obtain

$$E = \frac{dq}{dt}\frac{\rho}{2\pi z}\ln\left(\frac{r_2}{r_1}\right) + \frac{q}{2\pi c z r_1} + \frac{q}{2\pi c z r_2} \qquad [2]$$

with z an arbitrary system height. Upon solution and rearrangement of the above equation, we have

$$\eta_2 = \frac{E r_1}{r_1 + r_2}\left\{1 - \exp\left[-\frac{t}{\rho c \ln\left(\frac{r_2}{r_1}\right)\frac{r_1 r_2}{r_1 + r_2}}\right]\right\} \qquad [3]$$

The dissolution current, i_{diss}, is a function of the exchange current density, i_0, the transfer coefficient, α, the Faraday constant, F, and the overpotential, η, as given by Tafel behavior, $i_{\text{diss}} = i_0 \exp(\alpha F \eta / RT)$.[11] After combining the Tafel and overpotential expressions, we integrate over the pulse length and normalize by the length of the pulse and pause periods, resulting in the expression for the etch rate

$$\mathit{Etch\_Rate} = \frac{\int_0^t i_0 \exp\left(\frac{\alpha F}{RT}\frac{E r_1}{r_1 + r_2}\left\{1 - \exp\left[-\frac{t}{\rho c \ln\left(\frac{r_2}{r_1}\right)\frac{r_1 r_2}{r_1 + r_2}}\right]\right\}\right)dt}{\left(\frac{1}{m} + 1\right)t} \qquad [4]$$

where m is the pulse-to-pause ratio.

In Fig. 3a, the resolutions of stationary two-dimensional systems of varying tool radii and pulse durations are shown. In this case, resolutions were found at each tool radius and pulse duration combination by matching the etch rate characteristics of our computational model in the region near the leading edge of the moving tool: a steady-state etch rate of 1.5 µm/min (matching that of the tool) for a tool of radius 5 µm, 25 ns pulse, and 1:10 pulse-to-pause ratio, giving rise to a separation of 1.83 µm between the leading edge of

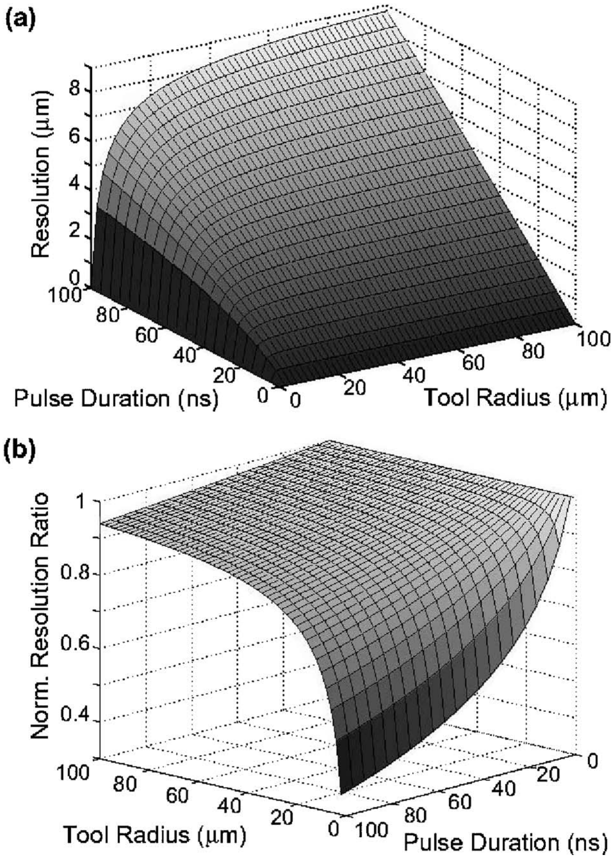

Figure 3. (a) Etch resolutions derived from a stationary two-dimensional model as a function of tool radius and pulse duration. (b) Ratio of etch resolution to pulse duration, normalized by limiting values at pulse durations of 0, for stationary two-dimensional model. Value of 1 indicates a linear increase in resolution with pulse duration.

the tool and the workpiece (d_2 in Fig. 1b). Despite the differences in workpiece geometries, the resolutions given here closely match the separations between the leading edge of the tool and workpiece for the computational model. For pulse durations of 50 ns or less, deviations are below 6% over the range of tool radii, owing to similar curvatures of the workpieces. With longer pulse durations, the deviations for smaller tool radii increase, but still remain below 13%. Due to this similarity, we can use the stationary model to gain insight into etching trends for regions with significant etch rates.

In Fig. 3b, the ratios of the above stationary resolutions to their respective pulse durations are shown, normalized by the limiting value at a pulse duration of 0 for the respective tool radius. Thus, regions where the normalized ratios approach a value of 1 see a nearly linear increase in resolution with pulse duration. As with the computational model, this occurs primarily in regions where the ratio of the resolution to the tool radius is small, such as for large tool radii or short pulse durations. In these regions, the system acts as a one-dimensional system, for which we can easily derive the linear relationship following the above treatment for the stationary two-dimensional case. Here, we assume the overpotentials at the tool and workpiece are equivalent and the resolution is of length x, giving

$$E = \frac{dq}{dt}\frac{\rho x}{yz} + \frac{2q}{cyz} \tag{5}$$

where y and z are arbitrary system dimensions. The evolution of the overpotential is then given by

$$\eta = \frac{E}{2}\left[1 - \exp\left(-\frac{2t}{\rho c x}\right)\right] \tag{6}$$

for which we obtain the etch rate expression

$$Etch\_Rate = \frac{\int_0^t i_0 \exp\left\{\frac{\alpha F}{RT}\frac{E}{2}\left[1 - \exp\left(-\frac{2t}{\rho c x}\right)\right]\right\}}{\left(\frac{1}{m} + 1\right)t} \tag{7}$$

If we consider a similar system with pulse duration nt and resolution nx, we find the etch rates are equivalent, and thus resolution scales linearly with pulse duration

$$\frac{\int_0^t i_0 \exp\left\{\frac{\alpha F}{RT}\frac{E}{2}\left[1 - \exp\left(-\frac{2t}{\rho c x}\right)\right]\right\}}{\left(\frac{1}{m} + 1\right)t} = \frac{\int_0^{nt} i_0 \exp\left\{\frac{\alpha F}{RT}\frac{E}{2}\left[1 - \exp\left(-\frac{2t}{\rho c n x}\right)\right]\right\}}{\left(\frac{1}{m} + 1\right)nt} \tag{8}$$

Additional numerical studies were performed using different capacity models for the electrochemical double layers (such as Gouy-Chapman-Stern), and the same linear trend for a one-dimensional system was found. In addition, we briefly note that to achieve a similar linear increase in resolution with pulse duration for a stationary two-dimensional system, the tool radius must also be scaled linearly:

$$\frac{\int_0^t i_0 \exp\left(\frac{\alpha F}{RT}\frac{Er_1}{r_1 + r_2}\left\{1 - \exp\left[-\frac{t}{\rho c \ln\left(\frac{r_2}{r_1}\right)\frac{r_1 r_2}{r_1 + r_2}}\right]\right\}\right)dt}{\left(\frac{1}{m} + 1\right)t} = \frac{\int_0^{nt} i_0 \exp\left(\frac{\alpha F}{RT}\frac{Enr_1}{nr_1 + nr_2}\left\{1 - \exp\left[-\frac{t}{\rho c \ln\left(\frac{nr_2}{nr_1}\right)\frac{nr_1 nr_2}{nr_1 + nr_2}}\right]\right\}\right)dt}{\left(\frac{1}{m} + 1\right)nt} \tag{9}$$

An additional stationary two-dimensional system was used to investigate the etch rate characteristics in regions of low etch rates, such as those at the full resolutions of our computational model. A system with the same characteristics as our earlier basis system was used to generate resolution data, only this time the targeted etch rate was that occurring at the full resolution downstream of the tool. Again the stationary model gave similar results to the computational model, generating etch resolutions within 3% for all tool radii above 0.5 μm. The associated normalized resolution ratios were largely similar to those of the earlier stationary model, with deviations of greater than 5% occurring only at a tool radius of 0.5 μm.

Thus far, we have looked at a deep vertical etch and a region away from both the initial workpiece surface and the bottom tip of the tool. Herein, we also examine a relatively low aspect ratio system where the effect of trench top and bottom edges becomes important. Figure 4a shows etch profiles from two-dimensional simulations of the initial vertical etch into the workpiece surface using a 2.5 μm radius tool and Fig. 4b shows the resulting resolution ratios for different pulse lengths at different etch depths. This result clearly demonstrates that the resolution ratios are a strong function of etch

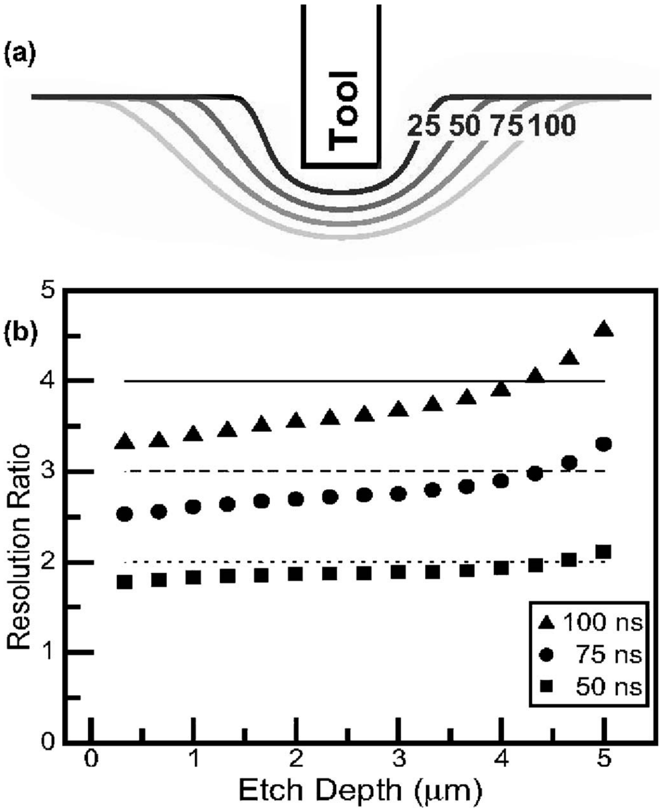

Figure 4. (a) Etch profiles for a tool of radius 2.5 μm etched to a depth of 5 μm. Pulse duration as indicated (ns). (b) Etch resolution ratios relative to that of a 25 ns pulse at varying etch depths. Horizontal lines indicate linear behavior.

depth, varying from sublinear to superlinear with pulse duration. While these ratios will likely change once lateral etching of the tool begins, they are an indication of the importance of the location of the measurement and demonstrate the range of resolution ratios which may be seen. Such precise analysis is unavailable experimentally at present, however the overall trend in the relationship between etch resolution and pulse duration is consistent with recent experimental observations.[10]

Conclusions

We have presented both analytical and computational models to examine systematically the effect of pulse duration on the etch resolutions of trenches in electrochemical machining with ultrashort voltage pulses. We found that the relationship between etch resolution and pulse duration is a strong function of tool radius and feature aspect ratio. High aspect ratio etching shows increasing degrees of sublinearity in etch resolution as pulse length is increased. This effect is offset if the tool radius is large enough to exhibit one-dimensional behavior; that is, the effect of tool curvature can be ignored. For low aspect ratio features where the effect of trench top and bottom edges is significant, the resolution-pulse duration relationship varies from sublinear to superlinear, depending on etch depth. This theoretical analysis, with comparison to experiments, demonstrates that we can gain many valuable insights into complex electrochemical reactions from a combined effort of theory and experiment, where no direct measurement of dynamical electrochemical processes is feasible using current experimental techniques.

Acknowledgments

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