



## Electrochemical micromachining of conducting stainless steel with ultrashort voltage pulse

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### ABSTRACT

An electrochemical pulse technique have been used to make micro holes on conducting stainless steel substrate. The method is based on the application of ultra short nanosecond voltage pulses where electrochemical reactions are locally confined with sub micrometer precision .Due to gentle removal of the material the grain structure of the material is revealed without any chemical and mechanical modifications. Electrochemical micro machining is based on the finite charging time of the electrochemical double layer capacity on the electrode surfaces due to the finite electrolyte resistance. The machining precision depends upon the electrochemical reactions and related to the pulse length. The design and fabrication of a unique electrochemical machining production system capable of micro and nano scale drilling have been presented for conducting stainless surface. Benchmarking prototype tool against existing micro and nano fabrication tool have been designed. The optimization of the process parameters, electrolyte concentration and solution conductivity have been presented.

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### Introduction

In recent years the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales where properties can differ significantly from those at larger scale has led to the design, characterisation, production and application of nanostructures by controlling shape and size at the nanometer scale. Various materials such as nanotubes, nanoballs, nanodots, and in particular nanoparticles<sup>(1-6)</sup> show an increasing interest due to their unique optical, magnetic, electronic, and chemical properties, which may differ greatly from those of the bulk material. Nanostructured materials have a great increase of surface area compared with the bulk material and the intrinsic properties of a particular material may be changed when it is finely divided. In, particular the use of nanoparticle modified electrodes presents advantages when compared with macro electrodes. Sometimes the complex process involves (i) Lithography (ii) Vapour deposition (iii) Ion implantation for integrated circuit chip manufacture.<sup>7</sup> Electrochemical methods either alone or in combination with others techniques have been developed for shaping materials<sup>8-10</sup>. A lithographic processes have been used in the fabrication of microelectro-mechanical systems for medicine, electro chemical sensors and actuators and chemical micro reactors<sup>11-14</sup> These process, now a common step of integrated circuit chip manufacture, incorporates electro deposition of copper interconnect metallization.<sup>15</sup> In this paper, we discuss a method in which high-resolution small scale features can be made solely via ECM means i.e., through localized anodic dissolution of a substrate

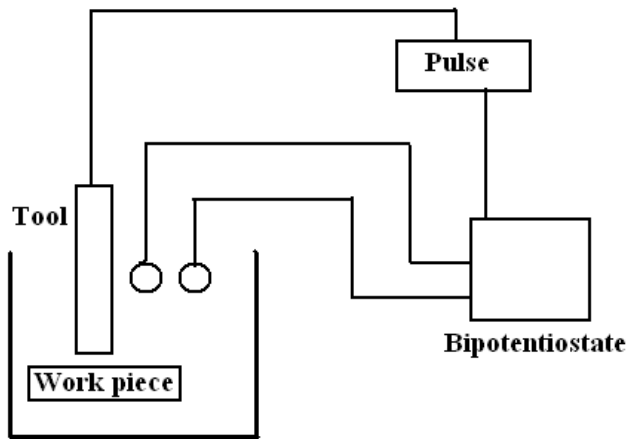
### Experimental and theoretical approach:

When the current flows between work and tool, the work is machined via the anodic reaction occurring there. If we consider the current path between tool and work piece there are capacitive

and faradaic currents as shown in Figure 1. The time constant for any current flow is given approximately by the product of the resistance of the solution of the current path and the capacitance near the electrode. (Double layer capacitance). If a current path is longer, time constant will be higher. But for ultra short voltage, the faradaic current can be neglected. Thus if ultra short voltages are used, the time constant will be less, the double layer charging is also restricted. An ultra Short voltage limits the changing of double layer capacitance to the vicinity of the tool. Small tools can be used to make small features. The problem is in resolution because the electrical field spreads in the electrolyte i.e., the current do not take the shortest path from tool to work piece. Using a D.C. current resolution is at best ten of microns, the anodic reactions occurs, over a larger portion of the work piece than desired. Therefore ultra short voltage can improve resolution<sup>16</sup>. By this method, patterns of any shape can be constructed with the appropriate tool.<sup>17</sup>

The potentials of the tool platinum and the work piece electrode were controlled with a potentiostat which kept the potentials between the tool and work piece constant by applying a potential to a Pt counter electrode and (Ag/ AgCl) reference electrode. All experiments can be conducted in an ideal electrolyte concentration is 4.5 M HCl with water.

The tool and the work piece are separated by Piezo actuators. The tool was fed into the work piece with a constant feeding speed avoiding mechanical contact between electrodes by monitoring the D.C. current between tool and work piece .All the samples were mechanically polished with (1200) grit sand paper followed by 1µm, diamond polishing solution .The samples may be washed with deionised water and dried with nitrogen gas and gap may be maintained at 0.2 µm.

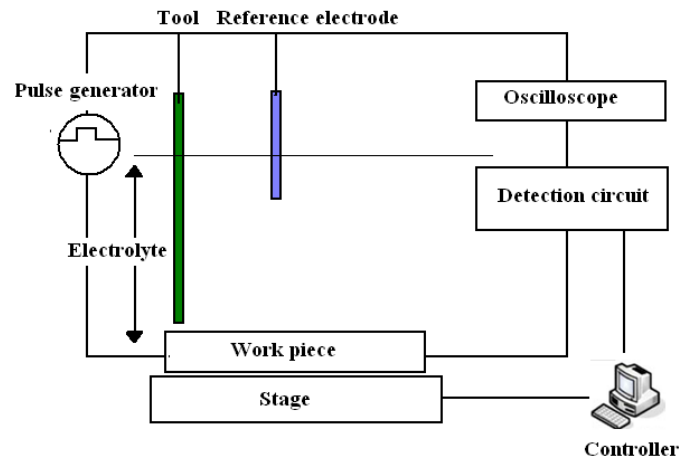


**Figure 1. Base line potentials diagram of work piece and tool Design of nano ECM machining:**

The fabrication of micro devices has become an important issue in modern technologies<sup>18</sup>. Various techniques were developed to fabricate such structures from semiconductors, metals, and polymers<sup>19-20</sup>. The micro mechanical devices are made from silicon by lithographic techniques. Three dimensional structures can only be achieved in several steps that is by a combination of lithographic techniques with electrochemical metal deposition<sup>21</sup>. Thus, for the micromachining of real construction materials like stainless steel few methods are available. One of the few methods is micromachining of alloys, stainless steel by the application of short voltage pulses of nanosecond duration to a tool electrode. This leads to the spatial confinement of electrochemical reactions to the nanometer level<sup>17</sup>.

Electrochemical reactions are driven by the potential drop across the electrochemical double layer in front of the electrode surface. This Double layer consists of ions a few angstroms in front of the surface and the respective charge in the metal electrode. It constitute of a plate capacitor with a very thin dielectric and a high capacity of the order of  $10 \text{ F/cm}^2$ . Upon application of the voltage the Double layer capacity is charged by the current flowing through the electrolyte, which has a finite specific resistance. The charging time of double layer becomes dependent on the electrode separation. Therefore with short enough voltage pulses the double layer capacity is only charged in electrode areas where the current path through the electrolyte is short enough, where the electrodes are very close. As the electrochemical reactions are dependent on the voltage drop across the double layer, electrochemical reactions or the dissolution of the material; are strongly confined to the charged regions of the double layer.

The platinum wire is used as a tool. The tool is perpendicularly mounted in front of work piece. With a piezo-driven stage the loop was moved in three dimensions with respect to the work piece. The tool and the work piece are dipped in an electrochemical cell with 4.5 M HCl as electrolyte. In addition a counter electrode of Pt and a Pd /hydrogen electrode are used as reference electrode to adjust the base potentials of the work piece and the tool. The experimental set up is well shown in figure 2.



**Figure 2. A setup of Micro and Nanoelectrochemical machining**

### Power Supply

Metal dissolution region is localized very near to tool electrode end using charging time difference between electric double layers at the tool bottom and side. Thus applying ultra short pulses between tool and work, faradaic dissolution current flows only in very confined regions. But for ultra short voltage, the faradaic current can be neglected. If ultra short voltages are used, the time constant will also be less, the double layer charging is also restricted. An ultra Short voltage limits the changing of double layer capacitance to vicinity of the tool. The oscillation frequency of cantilever can be measured in air by mechanical excitation of vibrations. The cantilever was electrostatically deflected by applying a D.C. Voltage (100-200 V) to a flattened  $50 \mu\text{m}$  diameter wire whose face is placed above the cantilever at a  $\mu\text{m}$  distance. Switching the voltage down to 10 volts, within about 100 ns resulted in oscillations of the tongue which were measurable as current oscillations across the varying capacitor formed by the cantilever and the deflection electrode. The amplitude of the capacitive current is proportional to the initial deflection of the cantilever. Super imposed on the oscillating current signal is an exponentially decaying background caused by the relatively slow recovery of the current measuring amplifier after the high voltage step<sup>18</sup>. The oscillation frequency measured amounts to 1 Hz. The dimensions of the tongue can be measured from the SEM images. Considering the power-law dependence of the oscillation frequency on the dimensions of the tongue, the calculated frequency is in reasonable agreement with the experimental one. The vibrations are performed in air only. As it is performed in air, the weak damping of the oscillations was observed. The vibrating cantilever provides a very sensitive microbalance. Such cantilevers could be machined from metal single crystals with specific adsorption properties. Thus applying the oscillation frequency (1 MHz for stainless steel) of 100 ns voltage pulses (2 V), the wire was fed  $30 \mu\text{m}$  into the work piece vertically, followed by lateral movement along a rectangular path<sup>21</sup>. An average potential of  $-0.2 \text{ V}$  of Ag/AgCl is found to be appropriate, because too negative potential at work piece led to slower the hydrogen evolution, which can interfere the machining process. Sufficient positive base potential at the tool can minimize the reactions due to faradaic current.

### Tool Design

Platinum wires are used for making the tool. Focused ion beam milling was used to fabricate tool electrodes. The platinum wire is first electrochemically etched and then focused ion beam

milling is done<sup>21</sup>. The platinum electrode is etched electrochemically in saturated solution of NaCl. capillary forces of the electrolyte form a meniscus around the wire when it is immersed into the electrolyte. In the meniscus the etching rate is enhanced and a necking phenomenon is observed. Finally, this part of the wire becomes so thin that can not hold the lower end of the wire, so the lower end breaks off and a sharp tip is left behind. The electrode was masked by an insulator.



**Figure 3. Electrode with 16  $\mu\text{m}$  circular end shape Electrolyte concentrations**

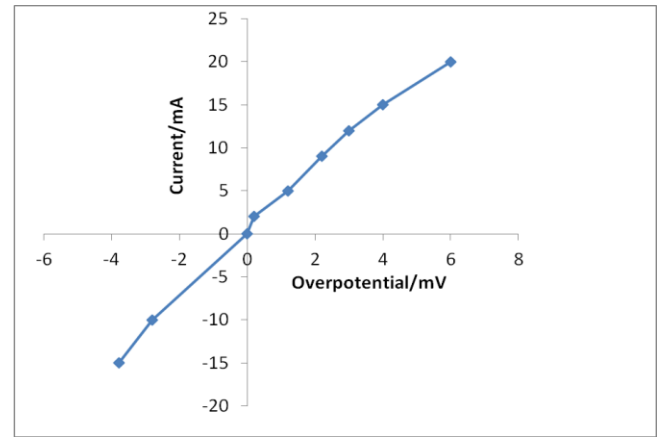
All experiments are performed in which the tool and work piece are placed in an aqueous HCl solution made with de-ionised water. These methods employ a tool held in close proximity one mm to a reactive anode electrode in the presence of an electrolyte and utilize ultrashort 50 nanosecond voltage pulses to modify the substrate surface selectively. The shape and feature resolution of synthesized structures would be determined by a complex combination of (a) charging and discharging of electrochemical double layers at electrode surfaces, (b) electrochemical reactions on the electrodes, and (c) transport of molecules to the electrode surface. Figure 2 shows a schematic of an electrochemical machining system. At distances on the micron scale, the voltage pulsing of the tool in an electrolyte leads to the charging and discharging of electrochemical double layers at both the tool and substrate. Electrically, this system can be thought of as two equipotential surfaces the tool and substrate in contact with spatially varying double layer capacitances. The known experimental values for pulse and pause durations, applied voltage, tool diameter were used. Double layer capacities and electrolyte resistivity were chosen to study which accompanied the experimental data and were equal to equilibrium values for the unperturbed experimental system. Edges and corners are rounded, and a separation of roughly 1.5 mm is seen between the tool and substrate at the substrate surface, tapering as one follows the sidewall to the trench bottom. The double layer capacities is 10 mF/cm<sup>2</sup>.

#### Dynamic Behaviour of Electrolyte

The role of the solvent is important in particular water, which can have a decisive influence even on ordered, specifically adsorbed ions in the inner part of the double layer. The highly dynamic structure of solvent and non-specifically adsorbed ions depends on the potential or surface charge density of electrode reactions is of key importance to electrochemical surface science. The dependence of current with over potential as shown in figure 4. It is clear from the figure that on increasing the current, overpotential increases significantly.

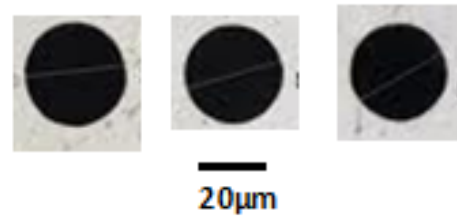
#### Microstructuring of conducting stainless steel workpiece

A corrosion resistant stainless steel grades 304 having 18% chromium, 8% nickel, density 8.00 g/cm<sup>3</sup>, electrical resistivity 0.072x10<sup>-6</sup>  $\Omega\text{m}$  and tensile strength 680 MPa was taken for machining. Mainly edge rounding shape, topology was taken into consideration. A solution of hydrochloric acid (4.5 M) was used as electrolyte.



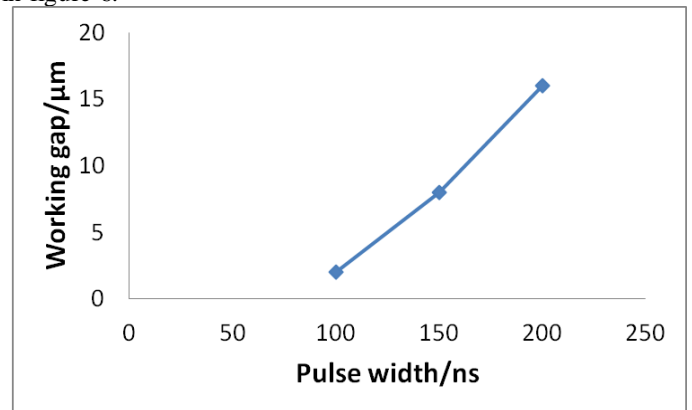
**Figure 4: Dependence of current with over-potential**

A hole of width of 20  $\mu\text{m}$  and a depth of 25  $\mu\text{m}$  were machined as shown in figure 5.



**Figure 5: A machine hole of 20  $\mu\text{m}$  and a depth of 25  $\mu\text{m}$ .**

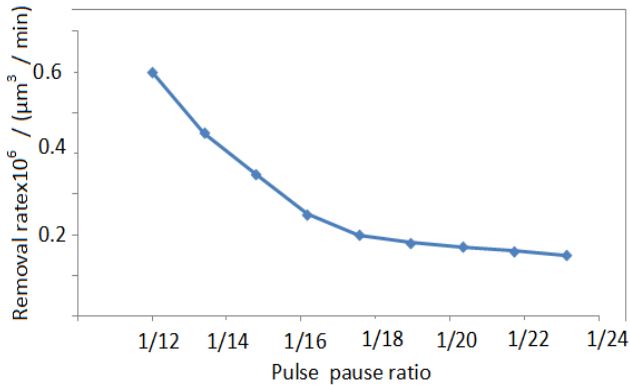
The plots of pulse width with working gaps is shown in figure 6. It is clear from the figure 6 that working gap shrinks with the reduction of the pulse width. The better manufacturing precision were at Amplitude = 3500 mV and pulse = 120 ns. The overview of the used parameters for the experiment shown in figure 6.



**Figure 6. Working gap over pulse width for amplitude = 3500 mV, Tool voltage = 120 mV Electrolyte = 4.5 M HCl, Current = 2500  $\mu\text{A}$  pulse pause ratio = 1/12 Tool diameter = 15  $\mu\text{m}$**

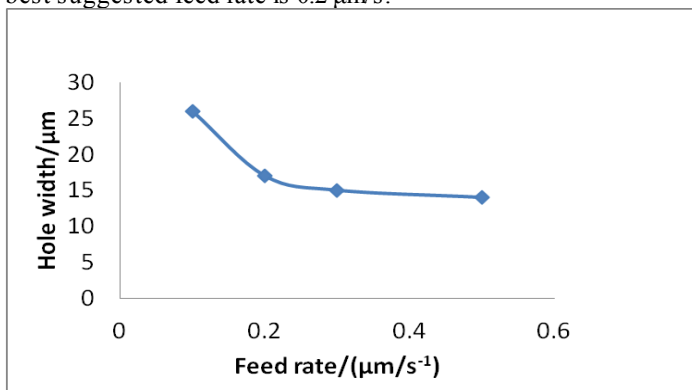
The variation of pulse–pause ratio from 1/12 to 1/22 was studied at zero tool voltage. An experiment with the potential at the tool has shown that a very low voltage leads to the best results in case of the optical considerations. But these low tool voltage could bring up some problems. When the drilling depth is higher, it can happen that the positive ions from the work piece treatment deposit at the tool. This deposition starts with a slight change of the tool geometry and can lead to a kind of ion based short circuit bridge between tool and work piece. Such a short circuit disrupt the manufacturing process. For the further experimental work the tool voltage was set at 120 mV to avoid

any unwanted occurrences. Figure 6 holes produced for the pulse–pause ratio experiment Figure 7 shows that the higher the pulse–pause ratio, the lower the removal rate. If within a period of time fewer pulses are applied, the charging and discharging of the electrochemical double layer also occurs less frequently. This is the obvious explanation for the low manufacturing speed of the holes made with a pulse pause ratio of 1/22. For this ratio the machining process was stopped because economic material removal could not be realized. The best combination of the optical quality of the surface and the removal rate was detected from a pulse–pause ratio of 1/12. The consequence was to fix this parameter for the next experiments.



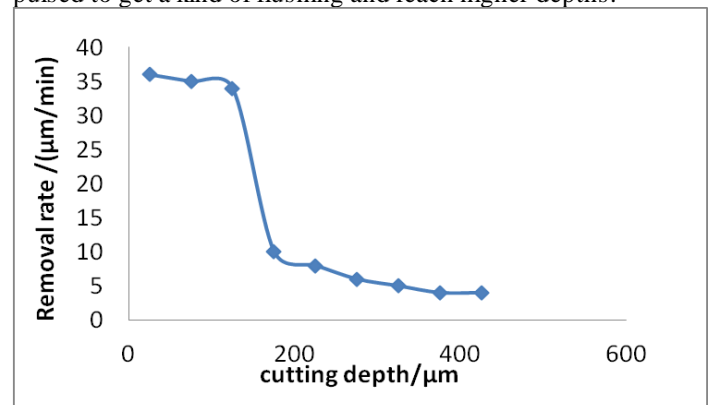
**Figure 7. Removal rate over pulse–pause ratio, Amplitude = 3500 mV pulse = 100 ns, Tool voltage = 0 mV, E = 4.5 M HCl, current = 2500  $\mu\text{A}$ , Tool diameter = 15  $\mu\text{m}$**

Machining conditions of this set of experiments were as follows: electrode diameter of 20  $\mu\text{m}$ , 4.5 M HCl electrolyte, pulse frequency of 1.0 MHz and machining voltage of 4.5 V, and feed rate varying from 0.1  $\mu\text{m}/\text{s}$  to 0.6  $\mu\text{m}/\text{s}$ . It is clear from Figure 8 that with the increase of feed rate, the holes width decreases. That is to say, the machining accuracy becomes higher as the feed rate increases. Increase of feed rate implies that the smaller inter-electrodes front gap can be achieved. In other words, with the increase of feed rate, average current density around the tool increases which leads to the increase of dissolution efficiency. So, the side gap could be much smaller. As shown in Fig.8, the holes width decreases rapidly in the range of 0.15-0.25  $\mu\text{m}/\text{s}$ , and with the further increase of feed rate in the range of 0.25-0.55  $\mu\text{m}/\text{s}$ , the hole width decreases less rapidly than in the range of 0.15-0.25  $\mu\text{m}/\text{s}$ . Therefore, the feed rate as high as possible under a steady machining process is proposed for the improvement of the machining accuracy. The best suggested feed rate is 0.2  $\mu\text{m}/\text{s}$ .



**Figure 8. Variation of hole width against feed rate other parameter are same as in figure 6**

A series of experiments was performed for all holes for machining with an adjusted depth of 25  $\mu\text{m}$ . This experiment was done to show how the manufacturing depth influences the process. Figure 9 shows that at a depth between 100 – 200  $\mu\text{m}$  the speed of removal rapidly reduces from above 40 to less than 15  $\mu\text{m}$  per minute. A possible explanation is that the electrolyte is not sufficiently available in the drilled hole. The electrolyte is sated in such depth, so the transport of new solved ions out of the bore slows down and the removal speed reduces. After the depth of around 300  $\mu\text{m}$  was reached, the process was stopped, because it was no longer possible to manufacture the work piece. To prepare sufficient electrolyte solution in such depth and thus realize better transport of the solved ions out of the bore, the mechanical movement of the tool inside the drilled hole could be pulsed to get a kind of flushing and reach higher depths.



**Figure 9. Removal rate with cutting depth. Amplitude = 3500 mV pulse = 100 ns Tool voltage = 120 mV, Electrolyte = 4.5 M HCl, Current = 2500  $\mu\text{A}$  pulse pause ratio = 1/12, Total diameter = 15  $\mu\text{m}$**

### Conclusion

A micromachining system for achieving micron-sized structures is developed. In order to obtain good machining accuracy and machined surface quality, the following rules should be observed. First, lower machining voltage, smaller pulse on time and minor diameter electrode can be used in the process to improve the machining accuracy. The feed rate as high as possible under a steady machining process is suggested. Successful fabrication of the microstructure proves that electrochemical micromachining is a promising micromachining technique which can be used to process the complex parts. It is assumed that the nature of tool and substrate double layers remains unchanged during electrochemical processing. However, we can expect that the properties of the electrochemical system will depend on the fundamental behaviors of solvated molecules in response to voltage pulses, particularly when the pulse duration is long and the applied voltage is high. This study shows the substrate double layer capacity plays an important role in determining the resolution of etched features. The double layer nature is largely determined by fundamental behaviors of solvated molecules.

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