

Nano Electro-Machining (nano-EM): A Novel Method for Sculpting Nano Vias (< 20 nm) for Nanoscale Packaging

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Abstract

There is a great need to produce nanoscale features on diverse and sometimes difficult-to-machine materials for electronic and bio-medical applications. This paper describes an electro-machining (EM) process at nanoscale, implemented using a scanning probe platinum-iridium (Pt-Ir) electrode tool (15-20 nm radius) in dielectric oil. The experiments were conducted by maintaining a gap of 2 nm between the tool and the work-piece. These experiments have successfully demonstrated that controlled and consistent machined features, as small as 10 nm in diameter, on atomically flat gold can be obtained. It is suggested that resonant tunnelling through dielectric oil molecules causes the removal of material.

Keywords: Electrical discharge machining; scanning tunneling microscope; nanoscale

Introduction

Nanoscale (<100 nm) machined features such as vias, cavities, channels, etc. are essential for fabrication of nanoscale integrated systems. Such structures can be used as z-axis blind and through vias for interconnects and templates for deposition of nanowires and nanojets [1] for next generation atomizers in micro fuel cells and proton exchange membranes (PEM) for fuel cells, single DNA detection devices [2] and molecular sieves for protein sorting [3]. One of the biggest challenges facing nanoscale machining [4] is to produce nanoscale features on diverse materials like gold, nickel, metallized polymers for electronic applications and on difficult-to-cut titanium alloys for bio-medical applications [4]. Hence, development of new processes capable of machining nanoscale features on a wide range of materials at low cost and high speed is essential. Various tools and processes such as scanning probe microscope (SPM) based indentation and scratching [5-6], nano-imprinting [7], focused ion beam (FIB) [8-9], femto-second laser [10], UV lithography [11], electron beam lithography (EBL) [12], and X-ray lithography [13] are being used for nanoscale material removal. Most of these techniques

primarily address the removal of silicon and polymeric materials. Currently, to the knowledge of the authors, there is no single process capable of machining precise nanoscale features and structures in hard and difficult-to-cut materials in a non-vacuum (e.g. liquid) environment at low cost. In light of this pressing need, a material removal (top-down) process utilizing electro-machining in a dielectric liquid medium offers a novel opportunity. The authors have used this concept to present a method where a scanning tunneling microscope [14] (STM) probe tip is integrated with material removal mechanism in a dielectric liquid medium. An STM tip operates in air and vacuum, and rarely under fluids like water. The novelty of the demonstrated process is in introducing a dielectric liquid medium of micro liter volumes between the Pt-Ir erosion tool and the work-piece surface. Also, unlike in previous research in the field of STM based machining [15] where the machining results were inconsistent, this approach demonstrates consistent machining of features as small as 10 nm. The process will hereafter be referred to as nano electro-machining or nano-EM. No special coating was required for the use of the STM tip under dielectric oil. STM metrology of the nano-EM machined features *in situ* was also conducted using

the same tool tip that was used for electro-machining.

Experiments

The nano-EM process was realized using a metal electrode tool (end radius $\sim 15\text{-}20\text{ nm}$ and made from Pt-Ir alloy) and a typical off-the-shelf dielectric oil (dielectric strength $> 41.2\text{ kV}/2.5\text{ mm}$). The electrically conductive probe and the work-piece were separated by a 2 nm gap and the STM was operated in a constant current mode during the machining process. The substrate was hydrogen flame annealed atomically flat gold grown using molecular beam epitaxy (MBE) on mica. A bias voltage of 10 V was applied for varying pulse on-time to the gold surface in dielectric oil as well as in air using in-house developed custom codes in the Nanoscript[®] software. After each pulse on-time time the system was switched to STM mode for metrological analysis. Thus, the standard on- and off-cycle was not followed, due to the current limitations of the system. A discharge current of 1 nA was maintained between the tool tip and the work-piece during the machining process. Precise control of the tunneling current by the STM instrumentation provided an accuracy of $1\text{ \AA}$ in Z axis (vertical) resolution and 2 nm in the X-Y plane. The resulting structures were analyzed using *in situ* STM imaging with the STM tip and the tip was analyzed using *ex situ* scanning electron microscopy (SEM) imaging. STM imaging of the gold surface was performed at a bias voltage of $100\text{-}300\text{ mV}$ and a tunneling current of 1 nA . The gold work-piece surface was imaged continuously to ensure that there was no surface reconstruction or machining at imaging bias. The comparison of STM scans in air and in dielectric medium showed no artifacts in the surface morphology due to presence of oil or scanning in oil.

Figure 1 shows a schematic of the nano-EM process with insets showing typical geometry of the active region of the nano tool tip, the liquid interface between the tool tip and atomically flat gold surface and the typical tip morphology. During machining the nano-EM tool tip was biased so as to cause negative tunneling currents, resulting in a flow of electrons from the nano electrode tool tip (referred to as electrode) to the substrate, analogous to the methodology used in macro scale EDM process.

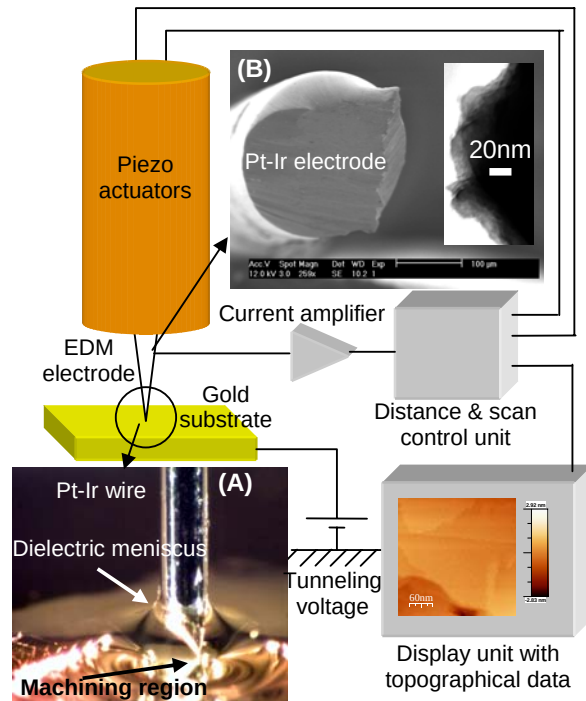


Figure 1: Schematic of the nano-EM set-up. A Pt-Ir electrode controlled using piezo-ceramic actuators was used for nano-EM of atomically flat gold on mica. Inset- (A) 70X optical micrograph of nano-EM electrode-oil interface. (B) SEM micrograph of electrode and a TEM close-up of tip showing atomic asperities for nano-EM. (www.physics.purdue.edu/nanophys/uhvstm/tip)

Analysis and Discussions

Figure 2 shows the effect of applying a voltage pulse of 10 V with three different pulse durations ($60, 90$ and 120 seconds) between the electrode and gold surface in dielectric oil. Hydrogen flame annealing of gold produces atomically flat islands of $\langle 111 \rangle$ orientation. The area of each atomically flat island is about 300 nm^2 . These flat islands are produced throughout the sample on different grains. STM scans show these islands on top of different gold grains. Unlike in air medium, the machining under dielectric oil was found to be uniform and consistent as evident from the STM scans. It is observed that even though machining is possible in an air environment (at similar voltages and not shown here), the results are inconsistent as observed by other researchers [15].

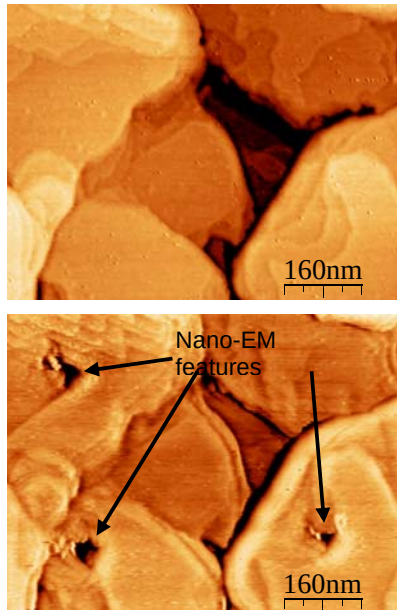


Figure 2: Nano-EM features created on atomically flat gold on mica grown using molecular beam epitaxy. The features were written by applying 10 V between a Pt-Ir tip and the gold surface for a time of 60, 90 and 120 seconds (starting bottom right going clockwise) in dielectric oil. Burr created by the process remains on the surface as currently the process does not have dielectric flushing.

The precision (discussed later) and consistency of machining in dielectric oil are the most notable observations when compared to previous studies [16-17]. Figure 3 (A) shows nano-EM of a ~1:1 aspect ratio feature on the gold surface. The cross sectional profile of via feature demonstrates well-defined material removal with 'V' shaped profile. The 2 nm discharge gap between the electrode and the gold substrate was maintained by the constant tunneling current. Thus, this 'V' shaped profile is the negative image of the electrode used for machining, similar to the machining observed in macro die sinking EDM. This will enable writing of vias for single DNA detection devices, nano templates on difficult-to-machine metal substrates, masks for nano-imprinting, surface plasmon lithography and other nano machining techniques. Figure 3 (B) shows the morphology of the re-deposited material generated during the nano-EM process. A re-deposited layer is also commonly observed in the macro [18] and micro discharge machining processes [19]. Currently, some of the material eroded by nano-EM re-deposits on the surface. The material removal rate increases linearly with time in the range of 30-240 seconds (Figure 4).

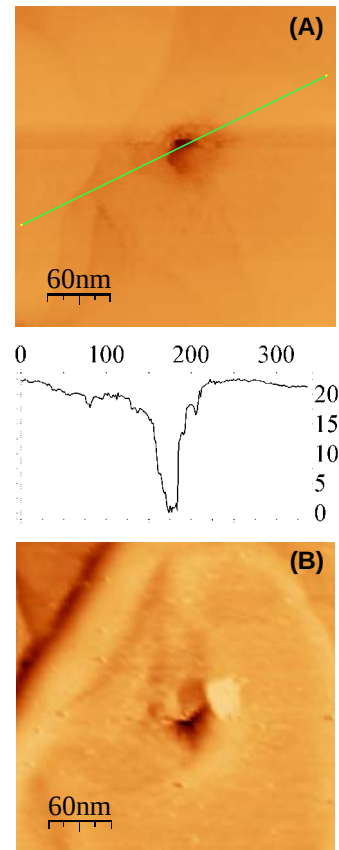


Figure 3: (A) Cross section of a nano-EM feature created at 90 seconds machining time with 10 V, 1 nA pulse. The section closely resembles the profile of the tip and electric field produced by it. (B) Nano-EM feature created at 240 seconds machining time and 10 V. The STM image clearly shows the re-deposited material, 'burr' close to the machined feature.

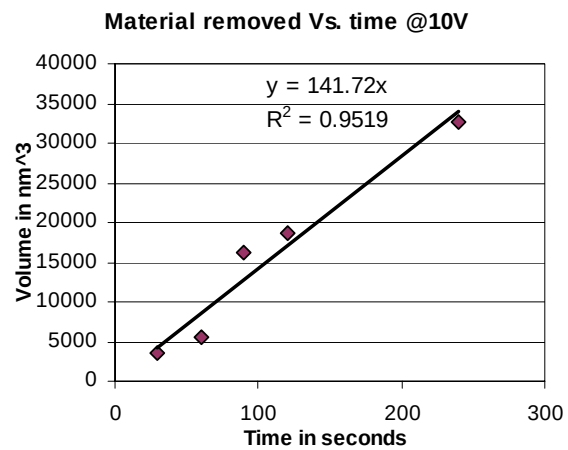


Figure 4: Volume of gold removed as a function of pulse width. The material removal rate increases linearly in the applied pulse width range.

The coefficient of regression is 0.95 suggesting a very good linear fit for the experimental data. Figure 5 shows the letter 'A' written on atomically flat gold under dielectric oil. Each feature is 10 nm in diameter and 0.6 nm deep. The authors believe that this demonstrates the capability of the nano-EM process to perform even sub-10 nm lithography on electrically conducting metallic surfaces like gold, titanium, chromium, chrome alloy, etc. at low cost and under ambient conditions.

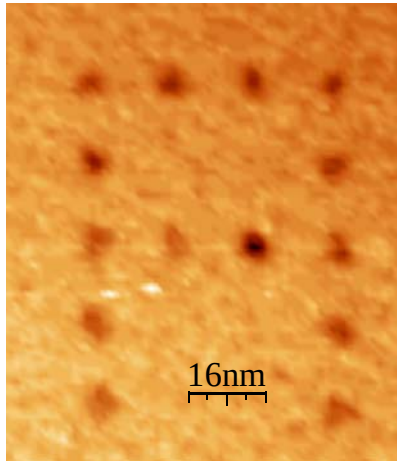


Figure 5: STM scan of the first letter of the alphabet "A" written on atomically flat gold under dielectric oil using Pt-Ir tips at 2.8 V and 0.5 seconds pulse width. Each feature is 10 nm in diameter and 6 Å deep.

The electric fields under the electrode were quantified in order to understand the process mechanism in dielectric oil vs. the reference air medium. In air, the electric field is of the order of 10^6 - 10^7 V/m for a 200 mV bias voltage. The breakdown voltage of air is 3×10^6 V/m. It is suspected that breakdown of air occurs when a voltage (10 V) one order of magnitude higher than the scanning voltage (0.1-0.3 V) is applied to the gold surface. In air, surface adsorbents such as water vapor, dirt, free radicals etc. cause variations in the morphology of the machined feature [20]. Water is an undesirable agent as a dielectric medium, since it readily absorbs impurities from air. When the electric field is applied, it immediately absorbs CO_2 from air forming complex carbon compounds, which degrade the quality of machining [21] especially when the electrolyte is not flushed continuously. In contrast, the dielectric oil is able to sustain higher electric fields (10^8 - 10^9 V/m), enabling consistent material removal. Macro and micro EDM [22] operate under electric fields of the order of 10^5 - 10^6 V/m. Fields of similar magnitude are created under an electrode

during normal STM scanning bias voltages. However, no machining or damage to the surface is observed during normal scanning in the dielectric media. As mentioned above, only an application of higher bias voltages yields the observed nanoscale machining.

Model of nano-EM

Several mechanisms [15-17, 23-24] have been proposed in the literature to explain material removal in air medium using high bias voltage STM, including mechanical contact between electrode tip and substrate, electro-migration, electronic contact, field induced electrochemical etching and field induced evaporation. In an intriguing observation, we could image the gold surface through the dielectric oil molecules, leading to the conclusion that the dielectric plays an active and unique role in the nano-EM process.

The possible mechanism in the present case is closely dependent on the state of the dielectric oil molecules in the tunneling gap between the electrode and the substrate. In the nano-EM process, the dielectric oil is a mixture of several organic compounds from C_9H_{20} to $\text{C}_{13}\text{H}_{28}$, the size of a molecule ranging from about 0.7 to 2.5 nm. The authors believe that there is an electric field assisted trapping and localized assembly of dielectric oil molecules between the electrode and the metal substrate. Further, the tunneling and associated energy transfer between the electrode and the substrate occurs through this dielectric molecular medium, potentially an anisotropic medium for charge transfer. Prior theoretical work predicts that charge transfer in a single alkane molecule (which is true for the used medium) occurs by resonant tunneling [25]. This resonant tunneling occurs via electron transfer between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) under the application of a threshold electric field. In nano-EM, the authors believe that the application of an intense bias results in resonant tunneling which provides the energy required for controlled material removal, and is a function of applied bias, current and pulse duration.

In order to model the process the tunneling phenomenon through the dielectric was divided into two regions of 'through bond' tunneling (electron transfer through bonds of dielectric molecules) and 'through space' tunneling (direct electron tunneling between the electrode and the work-piece). The material removal rate is directly proportional to the energy available for machining and hence on the magnitude of the tunneling current through the discharge gap. The tunneling current is directly proportional the square of the electronic transmission coefficient $T(E)$. The electron

transmission coefficient $T(E)$ is the ratio of flux of electrons which 'tunnel through' or 'transmit' through a quantum-mechanical energy barrier to the number of electrons incident on the barrier (For details refer [25, 26]). Hence in the case of nano-EM the transmission coefficient will represent the net energy transmitted from the electrode to the work-piece through the dielectric oil molecules and hence available for machining of the work-piece material.

$$T(E) = 4(1 - q^2) C_{eff}^2 (E)^2 \left[\frac{4Y^2 + (X - d)^2 - 4qY(X + d) + 4q^2Xd}{4qY(X + d) + 4q^2Xd} \right]^{-1}$$

Thus the tunneling current is directly dependent on the coupling term C_{eff} . The coupling term is given by the expression

$$C_{eff} = c + b^2 (E - w)^{-1}, q = (2d)^{-1} (E - e) \\ Y = (E - e), X = d^{-1} [(E - e) - C_{eff} (E)^2]$$

E , e , w are work functions of the tip, work-piece, and dielectric molecules, respectively in eV
 d is the thickness of the barrier (dielectric molecules) in Å
 c is the through space interaction coefficient
 b is the through bond interaction coefficient

Further experimentation and theoretical analysis is required to determine whether 'through space' or 'through bond' tunneling dominates the process. Authors expect, since there is no chemical bond between the dielectric molecules and electrode / work-piece, and there is a threshold below which machining is not observed; the process may be a nanoscale electric discharge driven machining (nano-EDM). Although, other mechanisms like field induced evaporation, electro chemical etching and electro-migration cannot be ruled out. Further studies are underway in order to understand the process mechanism and to predict the material removal rate as a function of applied voltage for a given dielectric, tip and work-piece material combinations. Another interest is to explore the viability of nano-EM towards nano-EDM using required process conditions.

Summary

The authors have demonstrated nanometer scale material removal, as small as 10 nm in diameter and 2 unit cells in depth using nano-EM. This process is predictable and controllable due to the key role of dielectric liquid medium, which the authors believe, provides an evidence for resonant tunneling in a molecular medium.

Acknowledgements

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Special Note

The work presented here has already been presented in the 55th CIRP General Assembly in 2005 ["Investigation of Nanoscale Electro Machining (EM)," Ajay P. Malshe, K. Virwani and K.P. Rajurkar, CIRP Annals, Manufacturing Technology, Vol. 54, No. 1, 175-78 (2005).]

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