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A comparative study of the dry and wet nano-scale electro-machining

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Abstract

In recent years, a nano-electromachining (nano-EM) process based on a scanning tunneling microscope (STM) platform has been demonstrated. Nano-EM is capable of machining nano-features, under both, liquid dielectric (wet nano-EM) and air dielectric (dry nano-EM) media. The objective of this paper is to present a comparative study between the wet and dry nano-EM processes based on process mechanism, machining performance, consistency and dimensional repeatability of these two processes. The comparison of the two processes has been conducted at near field nano-EM, where the gap between the tool electrode and workpiece is 2 nm and the machining is performed at room temperature and pressure (macroscopically). The major differences in the process mechanism are due to the media at dielectric interface, the breakdown field strength and breakdown characteristics of two dielectrics and therefore, the material removal mechanism. It is reported that the material removal mechanism of wet nano-EM is associated with field emission-assisted avalanche in nano-confined liquid dielectric, whereas, the material removal mechanism in dry nano-EM is associated with field-induced evaporation of material. The differences have also been observed in the machining performance, dimensions of the machined features and repeatability of the nanoscale machined features. The self-tip-sharpening process with the continuation of machining has added several advantages to dry nano-EM over wet nano-EM in terms of dimensions of the nanoscale features, repeatability and machining performance.

Keywords: Nano-electromachining; Wet nano-EM; Dry nano-EM; Process mechanism; Machining performance; Dimensional repeatability

1. Introduction

In recent years, to meet the increasing demand of manufacturing nanoscale-structures and features, a number of fabrication techniques have been developed, those can be broadly categorized into soft lithography, laser machining, and tip-based based lithography [1]. Some of the important applications of nanoscale features produced by these techniques are pores for DNA detection devices and electrical interconnects, jets for next generation fuel atomizers and controlled drug release, channels for controlled drug delivery and nano-fluidics and others [2]. In addition, these nanoscale-features can be used in fuel cells, molecular sort sieves and templates for deposition of nano-wires [1-2]. The above applications demand machining of features in wide variety of materials ranging from metal, ceramic, polymer and biological samples. So far, most of these nanofabrication techniques are driven for material removal primarily from silicon and polymeric materials, which are used in electronic and biological applications. However, with the growing demand from new applications, the fabrication of nanoscale features in different functional metals like gold, nickel, copper, titanium alloys are becoming more important, especially in optical, chemical and other applications [3]. There are several reported disadvantages of commonly used nanomachining processes; for example, residue buildup and contamination for nano imprinting process, material re-deposition for focused ion beam and femtosecond laser, photo resist or development residues for UV

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lithography and others [1]. Moreover, most of these processes are expensive in terms of cost per feature [1].

A nano-manufacturing process termed as "nano-electromachining (nano-EM)" has been demonstrated by the co-authors, which is capable of fabricating nanoscale features in conducting as well as difficult-to-cut materials [2]. The operational ability of STM in vacuum, air, and liquid mediums has enabled the development of nano-EM process in both liquid (wet nano-EM) [2] and air (dry nano-EM) media [4]. In nano-EM process, platinum-iridium [Pt-Ir (80:20)] or tungsten [99.9%W] is used as tool electrode, and atomically flat gold substrate or any conducting substrate such as carbon with atomic level surface smoothness is used as a workpiece. Liquid n-decane and air are used as dielectric for wet and nano-EM, respectively. The wet and dry nano-EM systems are comparable to the conventional micro- die-sinking electrical discharge machining (EDM) and dry EDM, respectively in terms of physical system components and their functionalities. EDM or micro-EDM process removes electrically conductive materials by means of rapid and repetitive spark discharges in the presence of dielectric medium between a tool and a workpiece [5].

Several research studies have been carried out on different aspects of wet nano-EM. Some of the reported studies on wet nano-EM are feasibility study of wet nano-EM [2], understanding dielectric breakdown and related tool wear characteristics in wet nano-EM [6], understanding behavior of machining interface and dielectric molecular medium [7], molecular dynamics simulation of wet nano-EM [8], and repeatability studies of wet nano-EM [9]. Moreover, in a recent study the authors reported mechanism and machining performance of dry nano-EM have been discussed [4]. Although both of these processes are found to be capable of fabricating nanoscale features with good dimensional repeatability and consistency, there are key differences between two processes in many aspects, which is focus of this work.

Therefore, the objective of the present study is to perform a comparative analysis between the wet and dry nano-EM processes. The comparison between the two processes has been conducted based on process mechanism, machining performance, consistency and dimensional repeatability of these two processes.

2. Experimental setup and procedure

A Digital Instruments (DI) Multimode Scanning Tunneling Microscope (STM) with NanoScope IV controller was modified to perform dry and wet nano-EM (Fig. 1). An atomically sharp conducting tool tip electrode was brought within 1-2 nm (operating distance) of the conducting surface for machining. A bias voltage, high enough to cause the breakdown of dielectric fluid at the gap between tool/tip and workpiece, was applied for electro-machining. In this study, hydrogen flame annealed atomically flat {111} gold grown using molecular beam epitaxy (MBE) on mica was used as a workpiece. The Pt-Ir (80:20) was used as a tool electrode material due to its stable performance and ability of retaining tip quality for long period. The nano-EM tools were fabricated by mechanical shearing and electrochemical etching. In case of wet nano-EM, n-decane was used as dielectric liquid, whereas for dry nano-EM, no intentional dielectric material was used at the gap between the tool tip and substrate workpiece, considering atmospheric air as a dielectric medium.

The dry and wet nano-EM were conducted in near field in a constant current mode. In near field nano-EM, the tip and the substrate were at the working distance of 1-2 nm. Precise control of the tunneling current by the STM instrumentation provided an accuracy of 1Å in Z axis (vertical) resolution and 2 nm in the X-Y plane. STM imaging of the gold surface was performed at a bias voltage of 100 mV and a tunneling current of 1 nA. The nano-EM was carried out at a voltage of 3200 mV and pulse duration of 1 sec for each nanoscale feature for both wet and dry nano-EM. The flowchart of the steps for nano-EM processes (dry and wet) is shown in Fig. 2.

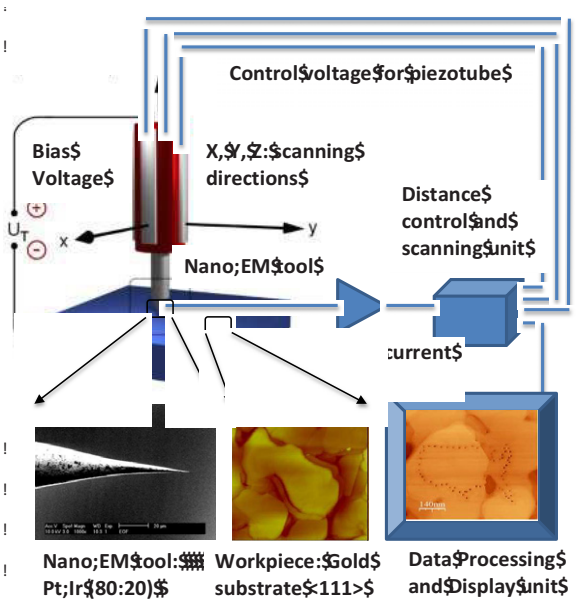

Figure 1: Schematic representation of the dry nano-EM setup [(a) SEM image of atomically sharp Pt-Ir (80:20) tip, (b) STM image of atomically flat {111} gold substrate and (c) machined "Map of USA" shown in the display unit (average hole size is 10 nm)]

The nano-EM tool quality has been evaluated in-situ using the current – displacement (I-Z) curves. The I-Z curve represents variation of the feedback tunnelling current from the tool as a function of the distance from the workpiece. In order to analyse I-Z curves, the mode of operation needs to switch to current – displacement spectroscopy, when the tool tip starts scanning over the sample workpiece. The in-situ tip evaluation process by I-Z curve and SEM analysis has been explained by the co-authors elsewhere in detail [10]. Figure 3 summarizes the definitions of the quality of the nano-EM tool tips by I-Z curves based on the dropping of tunnelling current to zero at different working distances.

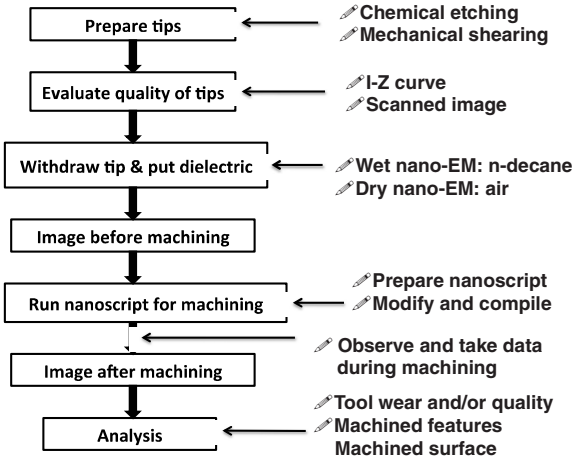

Figure 2: Flowchart showing the experimental procedure followed during wet and dry nano-EM

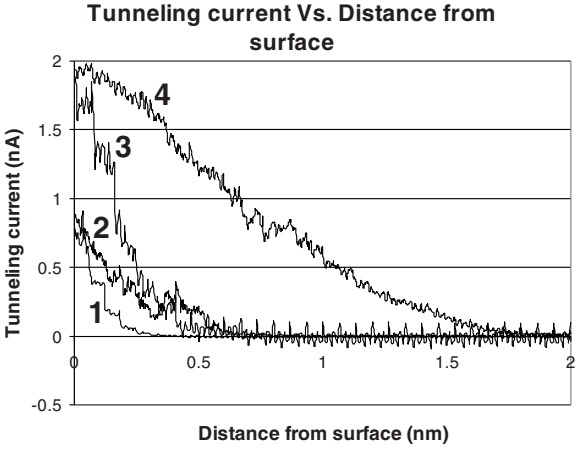

Figure 3: Typical current – displacement (I-Z) spectroscopy curves provided for different quality of nano-EM tools. (1: sharpest, end radii ≤ 30 nm, 2: end radii ≤ 50 nm, 3: end radii ≤ 100 nm and/or multiple asperities, 4: blunt tool (end radii ≥ 200 nm) [10]

3. Comparative study of dry and wet nano-EM

3.1. Material removal mechanism

During the wet nano-EM, material removal is associated with the dielectric breakdown of liquid n-decane. Upon application of bias voltage, high enough to generate field strength greater than the breakdown strength of liquid dielectric, electrons from both the tool and workpiece start to migrate into the tool-workpiece gap. These field-emitted electrons cause chemical ionization of the dielectric species inside the gap. Due to the ionization process at breakdown, there is generation of high current at a low resistance of the gap, which is known as "avalanche current". This increased avalanche current contributes to the breakdown of the liquid n-decane medium. The linearly increasing electric field strength required for breakdown of n-decane was measured to be about 1 x 10^9 V/m irrespective of the voltage polarity, and found to be independent of the cathode materials (W and Pt–Ir), unlike the EDM at macro and micro scales [11]. This phenomenon suggests that the dielectric breakdown in wet nano-EM is related to the confinement of the molecular dielectric in nanoscale gap and the net applied electric field stress. Upon dielectric breakdown, the gap acted as a short in the electrical circuit. The avalanche current flowing through a cathode shank diameter of about 100 nm resulted in a current density of 1.3 x 10^{13} A/m^2 causing heating, melting, and eventual vaporization of tool electrode [11]. Thus, upon breakdown the gap consisted of hydrocarbon, tool material, and gold atomic and molecular species. After withdrawal of applied voltage, the gap would recover its strength and fresh dielectric molecules replace the vapors in the gap. The summary of the mechanism of wet nano-EM is presented in Fig. 4.

On the other hand, in the dry nano-EM the atmospheric air is used as the dielectric medium. Upon the application of high bias voltage, there is sudden rise in the current at the gap width, resulting field-induced evaporation of materials from both the gold substrate and the nano-EM tool tip. It has been found that during the course of machining, the quality of the tool tip becomes better defined and sharper, and produced smaller and more consistent nanoscale features [4]. The improvement in the quality of the tool tip, also one can call "conditioning" of the tool tip; can easily be explained by the field evaporation principle. During the application of high bias voltage in dry nano-EM, there is intense local heating at the region of machining. Due to this intense heating, the materials get evaporated from the nano-EM tip, especially from different asperities of the tip. Nano-EM tip with multiple asperities exhibits I-Z curve with the dropping of current to zero at higher distance, thus making it comparatively inferior quality

for machining and scanning [10]. After machining about 50 - 100 nano-features, the field-induced evaporation of the multiple asperities takes place and the tool tip becomes sharper. Thus, in dry nano-EM the material is removed by field-induced evaporation resulting from heat generated due to breakdown of dielectric air. Fig. 5 presents the summary of the mechanism of dry nano-EM. However, the threshold voltage for machining may depend on relative humidity and the existence of critical humidity [12]. It has been demonstrated that the surface adsorbents like water vapor and free radicals may cause variations in the morphology of machined feature [13].

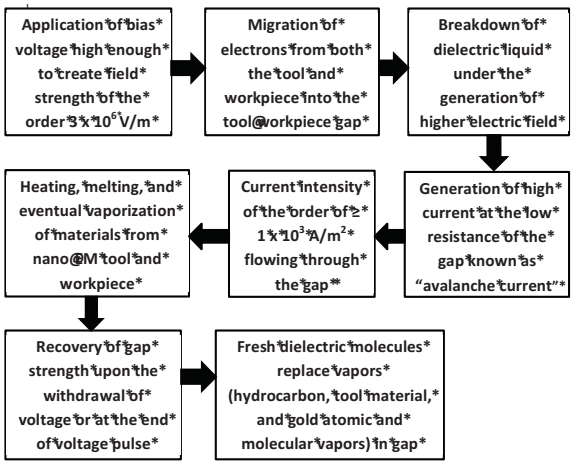

Figure 4: Summary of the mechanism of wet nano-EM

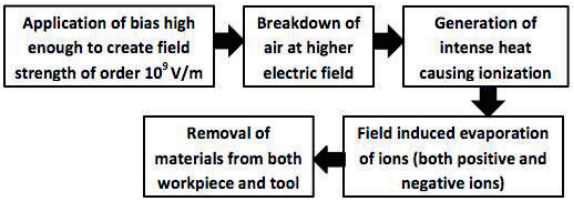

Figure 5: Summary of the mechanism of dry nano-EM

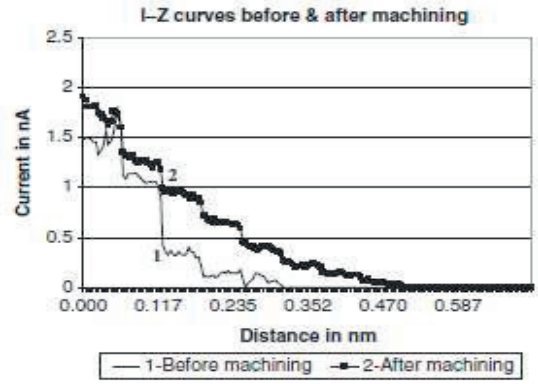

Figure 6: I-Z curves obtained from the same tool before and after machining 100 features in wet nano-EM [10]

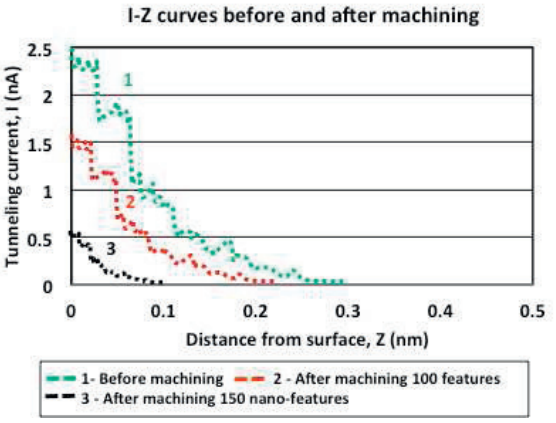

Figure 7: I-Z curves exhibited by same tool, 1: before machining, 2: after machining 100 nano-features, and 3: after machining 150 nano-features in dry nano-EM [4]

Although it is difficult to distinguish between the wet and dry nano-EM processes at nano scale, there are significant differences in the media of dielectric used, the breakdown voltage and characteristics of two dielectrics, and hence, the material removal mechanism. There is a difference between the field strength required for the breakdown of liquid n-decane dielectric and air dielectric, which may also contribute to the difference of material removal mechanism between the wet and dry nano-EM. The field strength required for breakdown of n-decane is about 1000 kV/cm or 1 x 10^8 V/m [14], which is much higher than that of air: 3 x 10^6 V/m [4].

Another significant difference is the change in nano-EM tool tip quality after two processes and tool wear mechanism. It has been reported that the tool tip quality decreases from quality 1 to quality 2 (Fig. 3) after machining about 100 nanofeatures in wet nano-EM as shown in Fig. 6 [10]. The blunting of the nano-EM tool is associated with the high current density flowing through the nano-EM tool during wet nano-EM, causing heating, melting, and vaporization of nano-EM tool [11]. On the contrary, the tip quality is found to improve in dry nano-EM after machining 100 features and it further improves after machining 150 features as shown in Fig. 7 [4]. The sharpening of the nano-EM tool tip in dry nano-EM is associated with field-induced evaporation of tool materials from the asperities of the tool tip [4].

3.2. Machining performance

The performance of the wet and dry nano-EM has been compared for machining letters "NSF" using the same parametric setting. Figure 8 compares the writing of same letters "NSF" using wet nano-EM [10] to that of dry nano-EM.

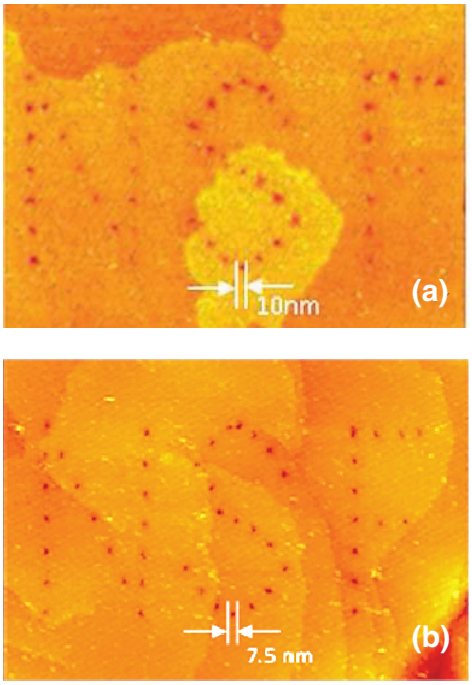

Figure 8: Machining of letters "NSF" using (a) wet nano-EM [10] and (b) dry nano-EM [4] with same parametric settings

It can be seen from Fig. 8(a) that, the dimensions of all the nano-holes are not consistent both in sizes and depths. However, it can be observed from Fig. 8(b) that almost all the holes produced in dry nano-EM is clearly visible. Moreover, very little variations in the dimensions and depths of nano-features are observed in dry nano-EM (Fig. 8b). The average diameter of nano-holes in dry nano-EM is found to be 7.5 nm for machining 50 holes in "NSF", whereas the average diameter of 50 nano-holes in wet nano-EM is reported as 10 nm for writing same "NSF".

Table 1 presents the comparison of the dimensions and repeatability of 50 nanoscale features fabricated by both wet and dry nano-EM. It can be observed from the column 2 and column 4 of the table that for using the mechanically sheared Pt-Ir tools, dry nano-EM provides lower values of mean dimension of the nano-features, lower standard deviations (S.D.) and lower spreading in all the directions, compared to that of wet nano-EM. This may be due to the fact that, the Pt-Ir tool has gone through the process of self-tip-sharpening by machining hundreds of nano-features before getting these results. The results suggest that the feature sizes are lower and more consistent in dry nano-EM. It can be seen that the results of dry nano-EM with mechanically sheared Pt-Ir tool are comparable to that of wet nano-EM using electrochemically etched Pt-Ir tool, as shown in column 3 and 4 of table 1. The dimensions of the nano-features are still lower in dry nano-EM. However, the lower standard deviation and spread percentage in X and Y direction in column 3 suggests more consistency of the nano features at the entrance for wet nano-EM with electrochemically etched tool. It can be seen that the consistency of features in terms of depths of the nano-features (Z direction) is still better for dry nano-EM (spread of 15.88% for dry nano-EM compared to 34% in wet nano-EM with etched Pt-Ir tool). In the fabrication of nanoscale vias for different applications, the consistency in depth is more important than that of dimensions in X and Y direction with tolerances.

Table 1: Comparison of the repeatability between the nano-features machined by wet nano-EM and dry nano-EM

Items	**Wet Nano-EM with mechanically sheared Pt-Ir (80:20) tool [9]**	**Wet Nano-EM with chemically etched Pt-Ir tool [9]**	**Dry nano-EM with mechanically sheared Pt-Ir tool [4]**
Features	50	50	50
X ± S.D.	8.724 ± 1.543	8.790 ± 1.030	7.528 ± 1.314
Y ± S.D.	10.352 ± 1.320	8.854 ± 0.880	8.077 ± 1.410
Z ± S.D.	0.403 ± 0.167	0.745 ± 0.250	0.639± 0.1015
Spread X (%)	18%	12%	17.45%
Spread Y (%)	13%	10%	17.45%
Spread Z (%)	42%	34%	15.88%

The comparison of machining performance for dry and wet nano-EM is presented in Fig. 9. It has been observed from Fig. 9 that the volumetric material removal is higher for dry nano-EM compared to wet nano-EM. For using the mechanically sheared Pt-Ir tool, the material removed is 2-3 times higher in dry nano-EM compared to wet nano-EM. The reason for low material removal rate in wet nano-EM is associated with the shallower depth of nanoscale features, when mechanically sheared tip is used. This can also be confirmed from comparing the spread of nanoscale features in Z-direction from table 1. In dry nano-EM, due to self-tip-sharpening process, the depth of the nano-features increases, which aids more volume removal. One important observation from Fig. 9 is that the volumetric material removal of dry nano-EM using self-sharpened mechanically sheared tip is comparable to the material removal in wet nano-EM using etched tip at the beginning of machining. As the machining continues, the cumulative material removal becomes higher for dry nano-EM. This is due to the fact that in wet nano-EM with etched tool, the tip quality is good at the beginning of machining. However, the tool quality deteriorates due to breakdown of n-decane dielectric, which makes the tool blunt and reduces the rate of material removal.

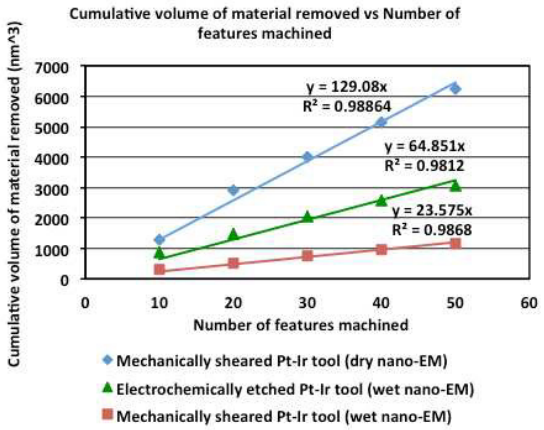

Figure 9: Comparison of cumulative volumetric material removal against number of machined features between wet nano-EM and dry nano-EM [4,9]

On the contrary, the tip quality improves as machining continues in dry nano-EM, which helps to maintain the material removal rate. As a result, the final cumulative material removal for dry nano-EM is about twice that of wet nano-EM under same parametric conditions.

4. Conclusions

A comparative study between the dry and wet nano-EM has been presented based on the material removal mechanism, machining performance, dimensional repeatability and consistency of the nanoscale features. There is considerable difference in the material removal mechanism between the two processes due to the differences in dielectric media, breakdown strength of dielectrics and tool wear mechanisms. The field emission-assisted avalanche in nanoscale confined liquid dielectric in wet nano-EM generates high current intensity resulting in heating, melting and evaporation of materials from both tool tip and workpiece. The material removal in dry nano-EM is associated with field-induced evaporation of materials. The field induced evaporation results in self-tip-sharpening process in dry nano-EM, thus improving the quality of nano-EM tool and machining performance, as opposed to wet nano-EM. For using mechanically sheared Pt-Ir tool and same machining conditions, the dry nano-EM provides higher material removal rate, smaller average dimension and higher depth of nanoscale features with better repeatability and consistency, especially for fabricating arrays of nanoscale features (100 – 150 features). Finally, the self-tip-sharpening process and longer nano-EM effective tool life make the dry nano-EM process more suitable for mass production and scale-up applications.

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