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Localized Electrochemical Deposition Using Ultra-High Frequency Pulsed Power

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Abstract

In this experimental study, localized electrodeposition of nickel pillars was performed to study the effect of pulse frequency, applied voltage, pulsed duty cycle, and the interelectrode gap, on the diameter of the deposit and the rate of deposition height. The effects of ultra-high frequency during the localized electrodeposition process, which have not been studied for micro electrochemical additive manufacturing purposes, are documented and further quantification of the effects of localization was conducted. It was found that the rate of deposition height increased with an increase in the pulse frequency, applied voltage, and duty cycle. As for deposition diameters, which is a measure of the localization, inter electrode gap was found to have no significant effect, while with pulse voltage and frequency, the average deposition diameter for certain parameters was substantially smaller than the tool electrode diameter, by approximate ratios of 2/3 and 1/5 respectively. These findings imply that modifying the electrical process parameters can allow for highly localized electrochemical deposition which is an important requirement for electrochemical additive manufacturing.

Keywords: Additive Manufacturing; Electrochemical Deposition; Localization; Miniaturization

1. Introduction

Many fields, such as medical, aerospace, military, and communications, have had an increasing demand of miniature devices with complicated microstructures. Ever growing number of applications, such as regenerative medicine, bionics, and microelectronics, are benefiting from additive manufacturing's capabilities of generating accurate features in 3D [1]. Additive manufacturing (AM) is defined as a process of bonding materials together to make parts, typically from computer-aided designed 3D models and most often layer upon layer [2]; and as opposed to lithography-based or micromachining approaches from the past, which struggle with the complexities of high-aspect ratios on micro scales, 3D microstructures produced through additive manufacturing provide an advantage in aptitude when it comes to functional and geometrically complicated parts using a diverse range of materials [3]. The two typical advantages to additive manufacturing over other manufacturing techniques are firstly, it allows the manufacture of components without many of the geometric constraints that tend to limit subtractive and formative processes; and secondly, being able to produce small quantities to meet the demands of customized components at a comparatively low average unit cost [4].

In the recent years, growing attention has been focused on AM, and great efforts are continuing to be poured into novel processes such as micro and nano scale 3D printing [5]. Once achieved in a viable and reproductive manner, this breakthrough will radically catalyze the face of technology in the aforementioned myriad of fields [5-8]. The furthering development of micro-electro-mechanical-systems has created the need for novel microfabrication processes, and among these, localized electrochemical deposition (LECD) stands out

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as a true 3D micro-rapid prototyping and direct-fabrication methodology capable of producing extremely high aspect ratio microstructures [9].

As one of many examples, LECD is a low cost, and one-step procedure, and is able to prepare from a single solution nanorods or films with varying parameters, making it a promising process for applications such as non-enzymatic glucose sensors [10]. In general, micro and nano scale 3D printing processes are providing rewarding alternatives to fabricating 3D complex conductive features based on conductive materials in an efficient and low-cost way [10], and though still a matter of research, LECD is one process that paves a promising path towards that future [11].

Electrochemical additive manufacturing (ECAM) is a novel localized electrochemical deposition process [12] is able to print free-hanging metal microstructures at room temperatures without thermal defects and without support structures [13]. In contrast, support structures and thermal defects area great found in other, traditional, AM methodologies. ECAM however is a process that has several parameters which can affect its results, and in this study, the parameters of duty cycle, voltage, frequency, and deposition gap, are experimentally explored to study their effect on the localization of the deposition in ECAM.

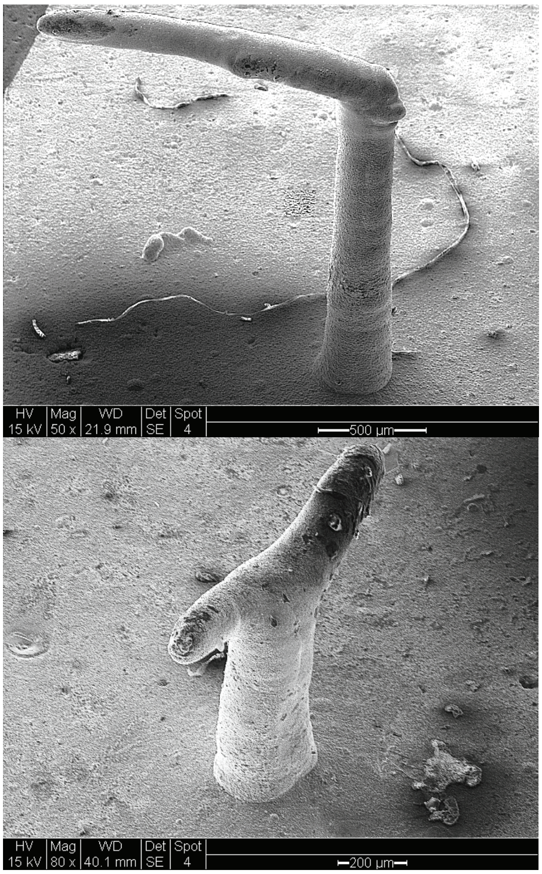


Fig 1: Examples of nickel parts made by ECAM using localized electrochemical deposition. Top figure is from [14]

2. Literature Review

Localized electrochemical deposition (LECD) was first demonstrated in 1996 [15], to produce 3D shapes, with the majority of the subsequent studies revolving around the process parameters which effected deposited structures and deposition rates [16]. A schematic explaining the LECD of nickel along with the respective electrode reactions is given in Figure 2. The potential applied between the electrodes needs to be above a threshold for electrodeposition to occur [17]. It has been reported that for the goal of attaining deposited pillars through LECD with compact structure, smooth surface, and uniform diameter, pulsed current conditions fare better than direct current conditions [18]. Additionally, LECD studies between two intermittently active electrodes have shown that voltage rather than distance has more influence on the surface morphology of the deposited columns [19]. Furthermore, in process-similar LECD experimentations, when depositing micro copper walls critical for micro-electro-mechanical-systems and semiconductor-related applications, it was discovered that deposition voltage and layer height substantially influenced the profiles of deposits and deposition rates [20]. Several other process parameters in LECD have also been studied by many research groups. In one such study, it has been shown that low voltages of 3.6 V with a small interelectrode gap (IEG) of 20 µm produce smooth surfaces with slow deposition rates, while high voltages of 4.6 V and a small IEG of 20 µm produce nodular surfaces with faster deposition rates [21].

Pulse current was found to produce a higher local current density, even though the average is the same as using a DC current [18]. Thus, the rate of deposition should not be affected, as that depends on the average current density. Pulsed deposition current was modelled based on analysing the transport of the cations and it was found that pulsed power resulted in higher peak current densities, due to the replenishment of the cations during the off time [22]. Pulsed power during LECD has been reported to produce parts with higher strength when compared to parts made using DC power [23].

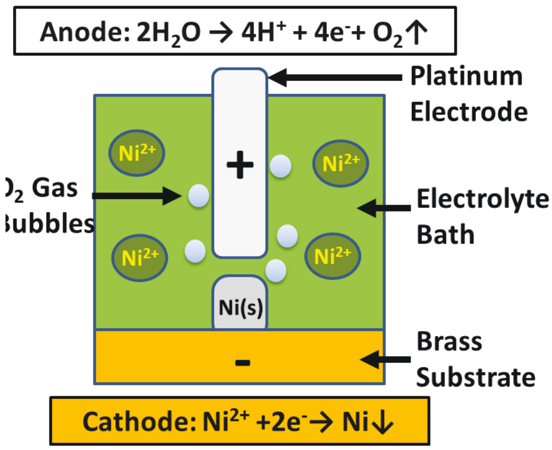


Fig 2: Schematic of localized electrochemical deposition of nickel

The reason for this was attributed to a unique microstructure with grains that contain a high density of layered nanoscale twins divided by coherent twin boundaries. The quality of the deposit was studied using an FEM based simulation study of the localized electrochemical deposition and it was found that the voltage, duty cycle, and interelectrode gap had significant effect on the deposit quality [24]. Localizing the deposition during LECD is difficult due to ion migration, which causes stray deposition on the sides leading to plating. Recent studies have investigated ion concentration in the electrolyte to predict the final profile of deposits after ECAM [25]. However, most of these studies are only qualitative, and do not predict the quantity of the deposit and plating.

Ultra high frequency (UHF) pulses were found to enhance the localization during the electrochemical machining process [26]. This is due to the impedance effect of the electrochemical double layer capacitance at higher distances between the electrodes. While these results are for the electrochemical machining process, no such UHF deposition attempts at the MHz range have been attempted for the electrochemical deposition process.

From this literature review however, it is clear that the effect of ultra-high frequency during the localized electrochemical deposition process has not been studied for micro electrochemical additive manufacturing purposes. In addition to this, it is also apparent that the effect of localization has generally not been quantified clearly in the literature. This work studies the effect of UHF on the localization of the deposit and the rate of deposition height.

3. Experimental Methods

An in-house built setup, shown in Figure 3, was used to perform experiments in this study; this in-house setup consisted of Precision Linear Stages from Physik Instrumente as the toolpath actuators, a TTI 50 Mhz function/arbitrary/pulse generator as the power source, and an Arduino Uno board used in conjunction with custom-coded MatLab scripts and Arduino commands as the microprocessor and software components. Table 1 provides the experimental parameters and their respective values.

Table 1. Process parameters.

Parameters	Values (s)
Applied Voltage	3 V, 4 V, 5 V
Interelectrode Gap	5 μm, 10 μm, 15 μm, 20 μm
Frequency of Deposition	10 kHz, 100 kHz, 1 MHz
Pulsed Duty Cycle	25%, 50%, 75%, 100%
Tool Diameter	250 μm
Tool Material	Platinum
Substrate Material	Brass
Electrolyte	Watts Bath
Temperature Range	20 °C to 25 °C
Pillar Height	1000 μm

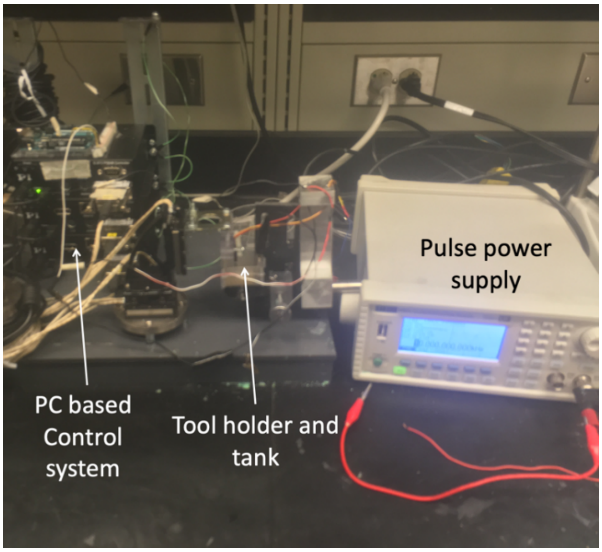


Fig 3: Experimental Setup

Four replicates of each experiment were conducted. The deposits were characterized using an optical microscope and a scanning electron microscope to measure the diameter and height of the deposits. The rate of deposition was calculated based on the current and stage motion data collected during the deposition by the Arduino and Matlab controls. Duty cycle is defined as the percentage of time the pulse power is on (t_{on}) to the total time period of the pulse (t_{on} +t_{off}). The average diameter and average deposition rate were measured and calculated from each set of experiments.

4. Results and Discussion

4.1. Effect of pulse frequency on the rate of deposition height and diameter of the deposit

Figure 4 and 5 show the experimental results of the effect of pulse frequency on the rate of deposition height and diameter of the deposit, and it is clear that the average rate of deposition height increases with an increase in the pulse frequency of the applied current. The duty cycle (50 %), IEG (10 μm), and voltage (5 V) were held at a constant value. This is however due to the steady state of the current density throughout the electrolyte near the cathode being reached more quickly as frequency increases [22], causing a more consistent deposition process, and simultaneously a more localized current density. During the deposition the cation gets depleted in the on-time and gets replenished in the off-time. This leads to a general decrease in the deposition current until a steady state is reached. This steady state is reached faster at higher frequencies as seen in our earlier modeling study [22]. This means that though the average current density throughout the entire system has stayed the same, the more condensed localization of the current itself in relation to the point of conduction/deposition has created a quicker deposition process since now the same average current density is filling up a more condensed space. Due to this same phenomenon, as pulse frequency increases, the average diameter of the deposition, as seen in Figure 5, decreases.

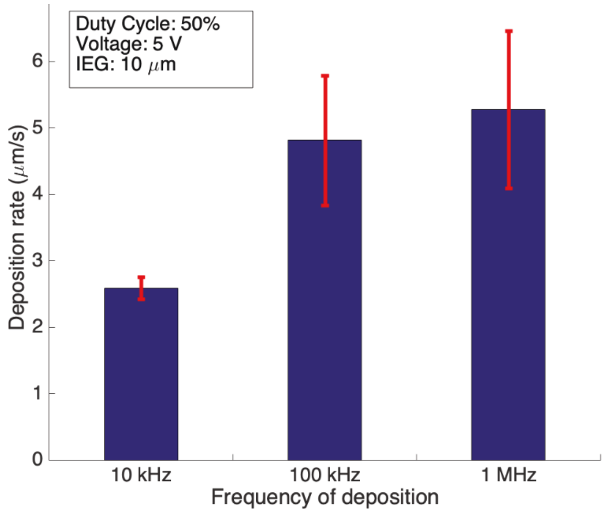


Fig 4: Effect of pulse frequency on the rate of deposition height

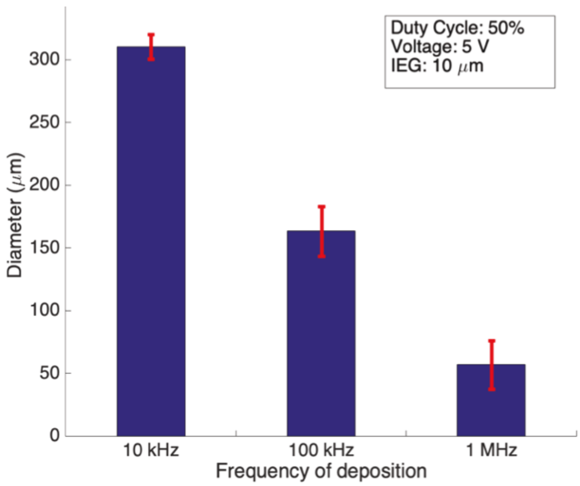
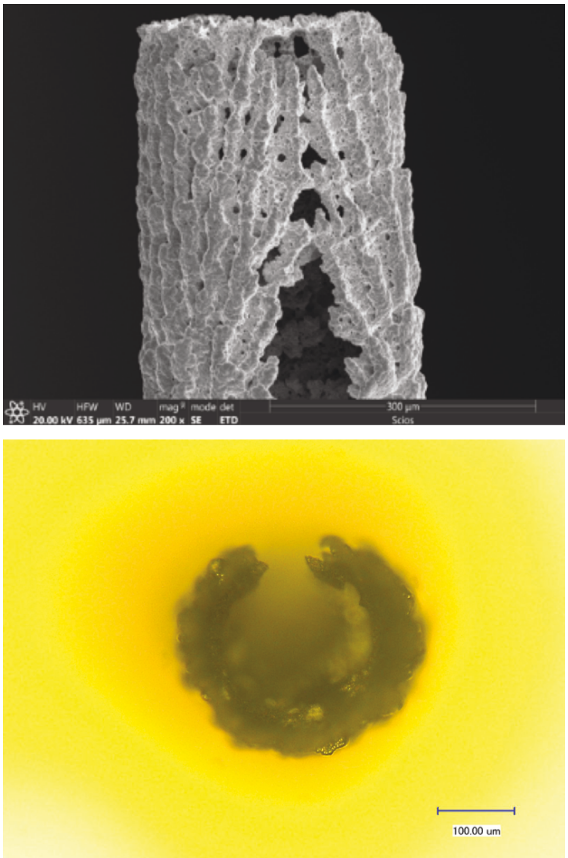
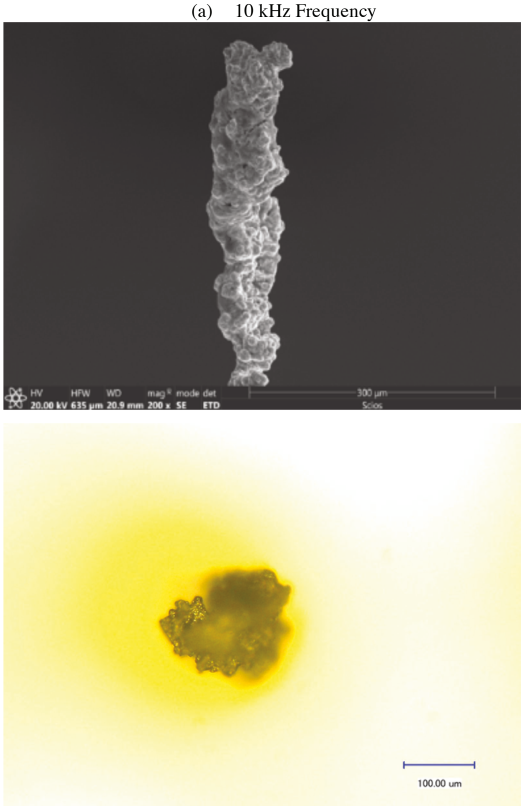


Fig 5: Effect of pulse frequency on the diameter of the deposition

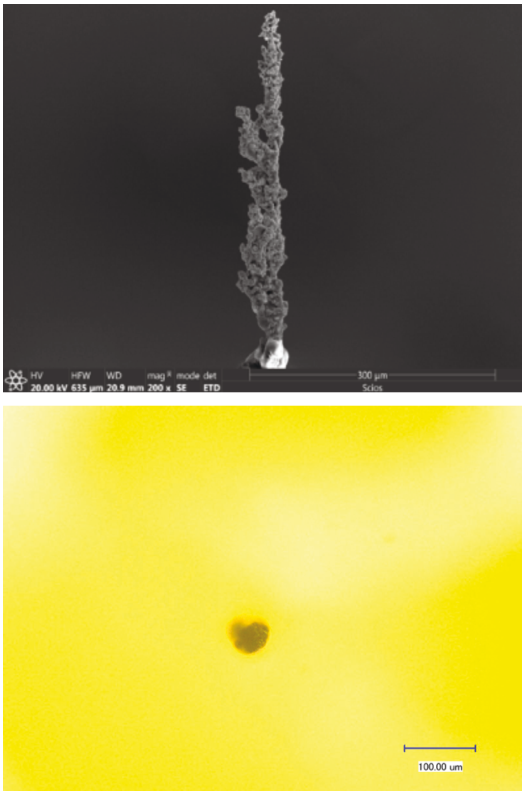
More interesting observation, however, is that as the pulse frequency of the applied current goes into the ultra-high frequency range of 1 MHz, the average diameter of deposition becomes approximately $1/5^{th}$ of the tool diameter. Figure 6 shows the images of the deposits made under varying pulse frequency deposition conditions using the same tool size.



(a) 10 kHz Frequency



(b) 100 kHz Frequency



(c) 1 MHz Frequency

Fig 6 Images of depositions made under different pulse frequencies

This reveals that in the ultra-high frequency range of deposition, high levels of localization can be achieved, even with a larger tool size. This phenomenon may be occurring because of the localization achieved due to the finite charging time constant of the double-layer capacitance, which varies approximately linearly with the local separation between electrode surfaces, and in-turn the polarization of the electrodes during ultra-short pulses causes electrochemical reactions to be confined to spaces where the electrodes are in the closest proximity as seen in the case of electrochemical deposition [26]. Only the section of deposit closest to the tool electrode receives most of the current with deposits further the tool electrode being denied the deposition current due to the electrochemical double layer. This finding shows clearly that the electrochemical double layer capacitance can be leveraged under UHF conditions to achieve highly localized depositions.

4.2. Effect of duty cycle on the deposit diameter and rate of deposition height

The experimental results on the effect of duty cycle on the deposit diameter and rate of deposition height are shown in Figures 7 and 8 respectively. Figure 7 shows that an increase in duty cycle of the pulse power results in increase in the diameter of the deposit. The trend reversed for the no pulse (100%) condition. This is due likely to the throwing power of the electrolyte being limited at lower duty cycle which causes the deposition to localize more.

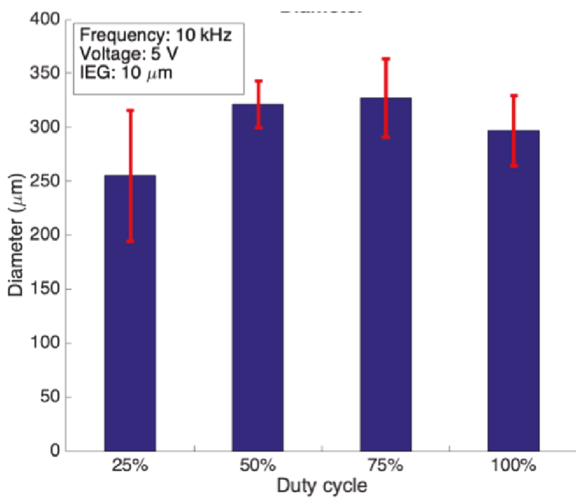


Fig 7: Effect of duty cycle on the diameter of the deposition

At longer duty cycle the pulse current is on for a longer period of time leading to the formation of stray faradaic currents resulting in a larger deposit size. The lowering of the deposit diameter at DC voltage might be due to the marginal reduction in the current density at DC voltages when compared to the pulsed current. This is due to the better cation availability due to the replenishment of the cations during the off time.

Additionally, as seen from the data from Figure 8, there is an increase in rate of deposition height as duty cycle is increased. The lower the duty-cycle, the lower the current density due to the long off time. Even though the peak current densities are higher at lower duty cycles the average current density is still lower at lower duty cycles leading to lower rates of deposition.

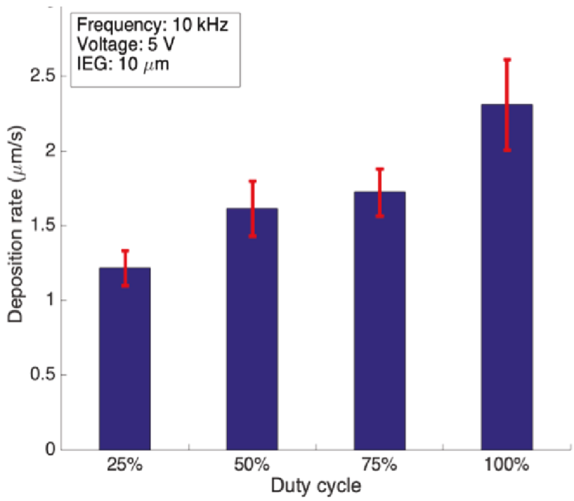


Fig 8: Effect of duty cycle on the rate of deposition height

4.3. Effect of applied voltage on the deposit diameter and rate of deposition height

The experimental results on the effect of applied voltage on the deposit diameter and rate of deposition height are shown in Figures 9 and 10 respectively. With an increase in the applied voltage, the current density in the electrochemical cell increases, thus causing higher rate of ion deposition on the cathode which results in increase in the diameter of the deposit as well as in the rate of deposition height.

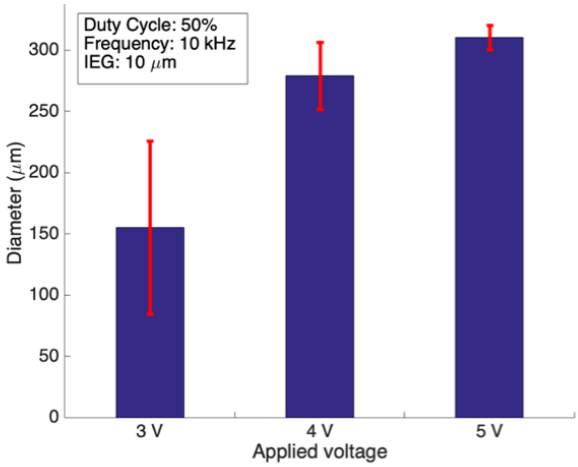


Fig 9: Effect of applied voltage on the diameter of the deposition

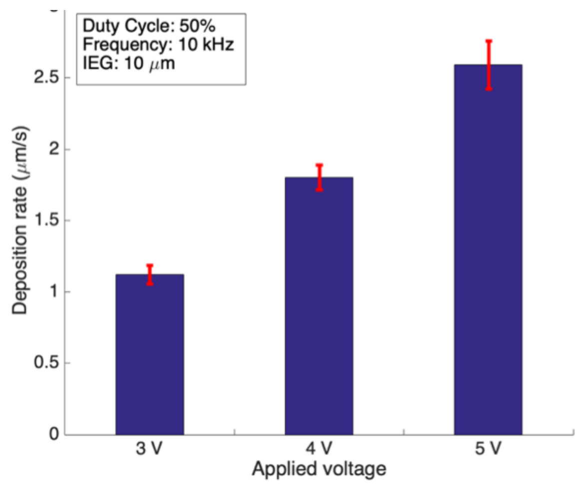


Fig 10: Effect of applied voltage on the rate of deposition height

4.4. Effect of interelectrode gap (IEG) on the deposit diameter and rate of deposition height

The experimental results on the effect of IEG on the deposit diameter and rate of deposition height are shown in Figures 11 and 12 respectively.

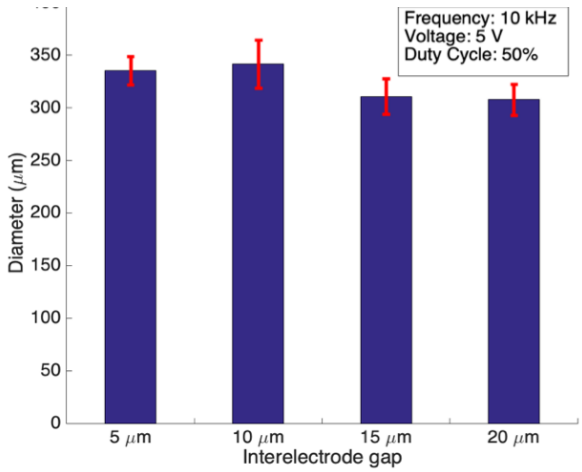


Fig 11: Effect of IEG on the diameter of the deposition

The IEG did not show any significant influence on the localization of the deposit diameter for the studied values of the gap. This matched with the prior current density estimation at the IEG which showed similar trends for these IEG values[14]. While earlier studies showed that the deposit quality measured as a distortion factor indicated poor quality at higher IEG none of them quantified the deposit diameter. Varying the IEG did not have a direct substantial impact on rates of deposition either, with the rate of deposit height growth staying between 1 – 2.5 μm/s similar to earlier simulation studies for non-pulsed conditions [14]. These results agree with the literature with the primary explanation being that the depletion region tends to fully form in the IEG leading to very similar rates of deposition under these IEG values. However, there is a decrease in the rate of deposition for the 10 μm IEG. This might be due to the depletion region forming fully in the IEG leading to slower deposition rates. This effect is not so pronounced in the higher IEG as the depletion region is not fully formed there, whereas at the smaller IEG the gap is small enough for the depletion region to not make a big effect on the deposition rates.

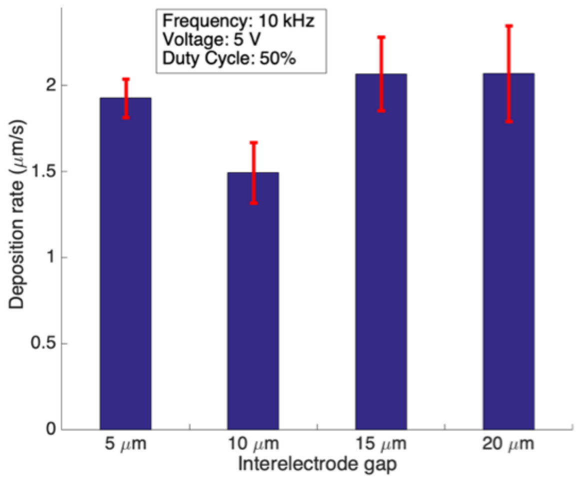


Fig 12: Effect of IEG on the rate of deposition height

5. Conclusion

Localized electrochemical deposition using ultra-high frequency pulsed power was performed in this study. It was found that deposits can be localized smaller than the size of the tool electrode while using ultra-high frequency pulse current. The double layer capacitance causing high impedance at regions farther from the IEG is believed to cause this localization. The rate of deposition height increased as the pulse frequency, applied voltage, and duty cycle, respectively increased. Deposits five times smaller than the tool electrode were achieved, which reveals the possibility of highly localized deposition even with larger tools when using ultra high frequency pulses. This finding provides pathway for nanoscale electrodeposition and nano ECAM even with a micro size tool.

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