Ultra-short time meniscus-confined electrodeposition at nanoscale

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Additive manufacturing, an evolving technology for crafting metal structures, holds the potential to supplant traditional precision manufacturing methods. Within this metal-based additive manufacturing landscape, electrodeposition-based techniques stand out for their ability to produce high-purity nanoscale structures (<100 nm). Meniscus-confined Electrodeposition (MCED), utilizing a nanoscale nozzle-equipped micropipette, offers effective confinement of the electrodeposition region. Nevertheless, the method grapples with nozzle clogging and persistent feature size constraints due to extended voxel deposition times. To address these challenges, we explored ultra-short time meniscus-confined electrodeposition, aiming to curtail deposition intervals for smaller voxel volumes, notably reducing voxel height. This approach holds promise in mitigating clogging and potentially achieving a breakthrough in feature size reduction. Our strategy involved a microcontroller for voltage generation, ionic current signal detection, and prompt electrodeposition termination. In practice, we successfully created a consistent 10×10 array of Cu dots, each approximately 100 nm in diameter, with a rising time of 2-4 ms.

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1. Introduction

Additive Manufacturing (AM), commonly known as 3D printing, is catalyzing a paradigm shift in the realm of structural design and fabrication. The utilization of 3D printing techniques for creating metallic structures has emerged as a pivotal facet of AM. This significance arises not only from its intrinsic capacity for unconfined geometric design but also from its vast potential to impart lightweight attributes and usher in cost-efficiency within mechanical frameworks[1]. Despite these promising prospects, the realization of sub-100 nm resolution in the printing of metal structures remains a formidable challenge. This is primarily due to the prevalent employment of energy-intensive methodologies in extant metal additive manufacturing processes[2, 3], where the amalgamation of metal powders is achieved through robust energy inputs. Consequently, this prevalent approach imposes an inherent limitation on achieving resolutions below 5 μm[2]. An alternative technique, namely Focused Electron/Ion-Beam-Induced Deposition (FEBID/FIBID), presents a distinctive capability to attain a remarkable resolution as fine as 10 nm[4]. However, it is essential to acknowledge that the structures deposited through this method exhibit notable deficiencies in terms of purity, attributed in part to the utilization of organic precursors in the deposition process[4, 5].

Recent advancements have led to the development of 3D printing techniques rooted in electrodeposition, employing either sharp tips or nozzles to realize highly pure nanoscale metal structures. In methods reliant on sharp tips, a probe typically housed within a scanning probe microscope system is immersed in a solution, and then subjected to nanosecond voltage pulses[6, 7]. This process yields exceedingly modest deposits and facilitates the attainment of features measuring below 100 nm. Meanwhile, nozzle-based approaches can achieve a minimum feature size of 25 nm through meniscus-confined electrodeposition (MCED) in air environments[8]. However, these methods encounter an obstacle in the form of clogging. This predicament arises due to the protracted duration of voxel deposition, despite each deposition lasting mere milliseconds. The preceding analysis underscores the significant potential of the MCED approach in achieving smaller feature sizes, contingent on resolving the clogging challenge. Specifically, controlling electrodeposition time to a shorter interval holds the key to diminishing the volume of each deposition voxel, especially its vertical extent. This strategic adjustment may solve the nozzle clogging.

In this study, we explored ultra-short time meniscus-confined electrodeposition at nanoscale to reduce the feature size of a single voxel, especially the height of a voxel. Moreover, it may be an efficient method to solve the clogging problem.

2. System Building

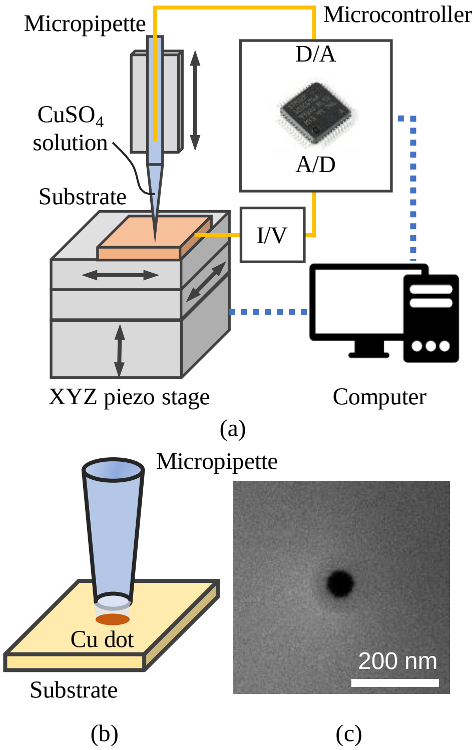


Fig. 1 (a) Diagram of a system for meniscus-confined electrodeposition. (b) Magnification diagram of the electrodeposition region. (c) Typical SEM image of a nozzle at the tip of the micropipette.

As shown in Fig. 1(a), a meniscus-confined electrodeposition system was built. It mainly consisted of a micropipette filled with electrolyte solution, such as 0.2 M $CuSO_4$ solution, an XYZ piezo stage that connected with an Au-coated Si substrate used as the cathode of electrochemical deposition, a Z stage for macro movement of micropipette and a microcontroller STM32 circuit which can apply voltage supply and detect ionic current signal. The microcontroller was programmed to apply different voltages according to the ionic current which is transferred to voltage by a weak current amplifier. All movements of stages and the microcontroller were programmed by computer. When a deposition process was started, a constant voltage, of 0.5 V was applied through a Pt electrode that was immersed in the micropipette. Then the micropipette moved close to the substrate with a speed of 0.01~0.1 μm/s according to the nozzle size. When the tip of the micropipette (nozzle) was close to the substrate enough without any contact, a liquid meniscus formed and an apparent pulse current appeared. In the meantime, the microcontroller detected the current from the substrate and judged whether the current was larger than the threshold. If the current is larger than the threshold, the microcontroller made the applied voltage to 0 V, so a voxel electrodeposition process ended. If not, a program loop continued until the current exceeded the threshold. Due to the fast processing speed of the microcontroller, shorter than 1 microsecond, the microcontroller can terminate the electrodeposition quickly. After the electrodeposition, the micro-controller communicated with the computer and then the approaching process was terminated, which was controlled by the computer. Fig. 1(b) shows that the diagram of an ultra-short time electrodeposition process and a Cu dot with a very small height. The diameter of the Cu dot was several nanometers to 100 nm, which was decided by the nozzle diameter (Fig. 1(c)).

2 Experiment Results

Fig. 2 shows the in-process monitored ionic current during a 10×10 Cu dot array fabricated by ultra-short time meniscus-confined electrodeposition. In Fig.2(a), the ionic current peak of Cu dots differed from each other in the range of 70 ~120 nA and every ionic current peak represented a Cu dot formation. Fig. 2(b) shows a magnification of the ionic current of the electrodeposition of a Cu dot in the red dashed box shown in Fig. 2(a). A 50 Hz noise current with an amplitude of about 5 nA was detected when a liquid meniscus didn't form. A short rising time (2~4 ms) was monitored and the peak amplitude of the ionic current was nearly 100 nA when the liquid meniscus formed. After the microcontroller terminated the electrodeposition, a decrease of current lasted 60~70 ms with a smaller gradient due to ionic absorption on the electrode.

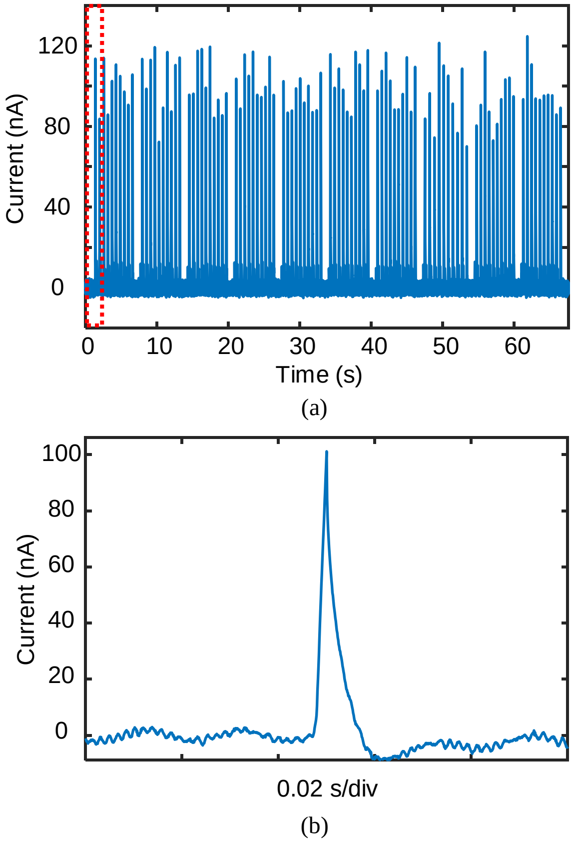
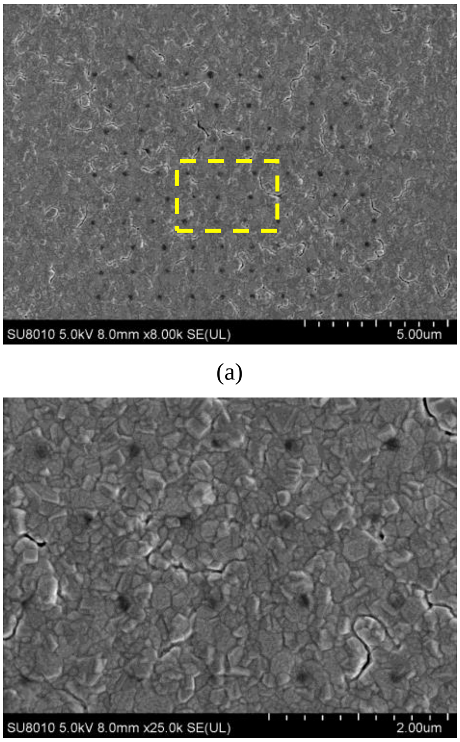


Fig. 2 (a) Ionic current during the electrodeposition of a 10×10 Cu dot array. (b) Ionic current of the electrodeposition of a Cu dot.

Fig. 3 shows that a 10×10 Cu dot array was fabricated on the substrate and the magnification image was shown in (b). The shape of Cu dots had a high consistency and the diameter of Cu dots was approximately 100 nm. The height of Cu dots was hardly measured directly from SEM images. Atomic force microscope (AFM) was used to measure the height of Cu dots, but it was also hardly measured for the substrate was a little rough. Thus, a smoother substrate should be made for a future

AFM measurement or transmission electron microscope (TEM) may be applied to measure the height of Cu dots but sample preparation may suffer a big challenge.



(a)

(b)

Fig. 3 (a) SEM image of a 10×10 Cu dot array. (b) Magnification SEM image of (a).

3. Conclusions

In conclusion, we explored the ultra-short time meniscus-confined electrodeposition using a microcontroller to generate a voltage supply, detect the ionic current signal, and most importantly, terminate the electrodeposition as soon as possible. Short ionic current rising time (2~ 4 ms) was monitored in the experiment. SEM images also show a high consistency of a 10×10 Cu dot array with a diameter of approximately 100 nm but the height of dots cannot be easily measured by AFM, which should be studied as our further work.

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