



Synthesis of crystalline metal nanomonoliths by e-beam reduction of negatively electrified jets



J.S. Fisher^a, P.A. Kottke^a, A.G. Fedorov^{a, b, *}

^a George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

^b Parker H. Petit Institute for Bioengineering and Bioscience, Georgia Institute of Technology, Atlanta, GA 30332, USA

ARTICLE INFO

Article history:

Received 18 May 2018

Accepted 28 June 2018

Keywords:

Liquid phase focused electron beam

–induced deposition (LP-FEBID)

Direct-write nanofabrication

Electrospray

Nanocrystals

Silver

ABSTRACT

Direct writing of nanoscale structures with focused electron beam–induced deposition (FEBID) is a promising route to atom-by-atom growth of complex three-dimensional nanostructures, but application has been constrained by slow growth rates (largely due to low precursor density), a limited selection of non-carbonaceous precursors, and a highly carbonaceous material composition resulting from the dissociative decomposition growth mechanism and organometallic precursors used in gas-phase FEBID. In this article, we report on the discovery of a new mode for liquid phase FEBID that enables growth of large metallic crystalline monoliths at exceptionally high growth rates ($>1 \mu\text{m}^3/\text{s}$) from water-dissolved metal salts using nanoelectrospray-induced non-equilibrium electrochemistry. Deposit morphology is controlled using the bias of the electrospray, with negative electrospray promoting crystallinity (as opposed to positive electrospray which results in granular deposits). Crystallinity is further promoted by elevating the pH of the electrospray solution. This approach opens a pathway for rapid direct writing of larger-scale monolithic metal structures using an electron beam.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Three-dimensional direct-writing techniques, when applied to fabrication of complex nanoscale and mesoscale structures, would benefit tremendously from the ability to control deposit structural characteristics, such as crystallinity. Control of crystallinity is a long-standing goal of nanoscale materials research due to general improvements in a number of critical transport properties with increasing grain sizes and reduction in grain boundaries, i.e. increased thermal and electrical conductivity of nanoscale materials [1–3]. As vividly stated in a recent review [4], electron/ion-beam based deposition methods have the potential for “full control of atomic arrangement and bonding in three dimensions”; yet, the practical realization of this tantalizing possibility has been elusive, confined to deposition of predominantly carbonaceous structures from gas-phase precursors. Recent progress in developing computer-aided design (CAD) tools and using them for automated growth of three-dimensional (3D) complex, computer-controlled nanostructures via gas phase focused electron

beam–induced deposition (FEBID) is remarkable [5,6] and further motivates to expand the capabilities of FEBID to a broader set of precursor chemistries and phases, aiming to achieve higher growth rates, and more importantly, greater control over the deposit composition and microstructure. In this article, we report on a discovery of a new pathway for electron beam–directed rapid growth of monolithic metal deposits, with crystal sizes on the order of several micrometers. Although the deposits are topologically simple, the approach can be extended to growing more complex structures. The foundation of the process is the use of nanoelectrospray to assist focused electron beam–induced deposition. This process, nanoelectrospray-assisted focused electron beam–induced deposition (NESA-FEBID), enables the rapid growth of amorphous carbon structures (pillars and suspended bridges) and simple, large granular metallic pillars [7]. Here, we describe a newly discovered method to control the morphology of metallic deposits, with structure varying from a highly granular assembly of nanoparticles to fully crystalline as a result of the combined effects of nanoelectrospray bias, i.e. positive or negative electrospray, in combination with sprayed solution pH.

Traditional e-beam synthesis techniques involve electron beam promoted decomposition of gas-phase precursors to grow either metal or carbon deposits on the surface of a solid substrate. In the

* Corresponding author. George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA.

E-mail address: AGF@gatech.edu (A.G. Fedorov).

past several years, it has been demonstrated that electron beam–induced deposits can be grown from liquid-phase precursors at a liquid/solid interface with (1) encapsulation of the liquid, e.g. WetSEM capsules (Quantomix) or liquid cell transmission electron microscopy (TEM) [8–14], (2) condensation of water vapor in an environmental scanning electron microscopy (ESEM) environment [15], (3) creation of a liquid pool by contact of the substrate with a liquid-containing capillary [16], or (4) through establishing a film with a liquid jet, as previously demonstrated by our group utilizing nanoelectrospray [7].

Liquid phase focused electron beam–induced deposition (LP-FEBID) promises significantly higher deposition rates, but a review of the published literature indicates that large LP-FEBID deposits (greater than $\sim 0.5 \mu\text{m}$) exhibit highly granular structures [9,16], while only very small deposits grown in liquid containing TEM cells no thicker than a few hundred nanometers are predominantly crystalline [12,13]. This highlights the importance of (1) understanding the mechanisms involved in LP-FEBID deposit growth and (2) developing methods to control conditions and therefore steer growth via the desired mechanisms to obtain crystalline deposits from rapid LP-FEBID. We hypothesize that growth of highly crystalline deposits in a liquid domain is facilitated if nanoparticle formation is hampered and conditions for electrochemical growth of metal particles are promoted. Thus, conglomeration of rapidly forming nanoparticles would be avoided in favor of crystalline growth of monolithic metallic deposits. In this article, we present a new pathway to e-beam–mediated growth of large crystalline metallic nanomonoliths, in which negative-mode electro spray prevents formation of nanoparticles prior to e-beam irradiation and produces conditions in which an excess of anions inhibits excessive nanoparticle formation by the electron beam, while higher pH promotes a crystalline growth mode.

2. Methods

All deposition experiments were performed using a FEI Quanta 200 scanning electron microscope with a tungsten filament, operating primarily at a 30 keV accelerating voltage and a current of 3.5 nA (spot size 6). Liquid films were formed using glass capillaries with a 2- μm tip pulled in-house using a Sutter P2000 capillary puller from 1 mm outer diameter capillary stock (Sutter). The voltage in the electro spray experiments is sourced from a high-voltage power supply operated in a range of 300–700 V (Stanford Research Systems PS350), with beam and electro spray current measured through a wire attached to the stub support using a picoammeter (Keithley 6485), which is otherwise electrically isolated from the scanning electron microscope (SEM). Spray currents vary significantly based on solute concentration but are typically observed in the range of a few nA.

All experiments were performed using solutions prepared from chemicals of the same origin—high-performance liquid chromatography (HPLC)-grade deionized water (Fisher Scientific) and high-purity silver nitrate and sodium hydroxide salts with trace metals (Sigma-Aldrich). To target multiple pH and salt concentrations in the solution to be sprayed, multiple concentrations of sodium hydroxide in water and silver nitrate in water are prepared and mixed with deionized water to produce solutions of silver nitrate, sodium hydroxide, and water, where the effective pH is based on the concentration of sodium hydroxide in the spray solution. Solutions of sodium hydroxide in water are prepared in 1 pH intervals (8, 9, 10, etc.), and solutions of silver nitrate in neutral water are prepared at elevated concentrations (10 mM and 100 mM). The pulled glass capillaries are back-filled with a thin fused silica capillary attached to a syringe, ensuring no visible bubbles at the tip through inspection. The capillary is sealed in a

custom built spray cartridge, with a platinum wire electrode fed through the sealed cartridge to within a few mm of the tip. The cartridge is mounted to the SEM stage with dielectric 3D-printed components to ensure best fit within the SEM chamber. The capillary tip is angled downward and manually positioned to within a few hundred μm of the substrate while the chamber is open. The substrate is silicon with a native oxide layer diced into 1 cm squares and mounted onto an aluminum SEM stub with carbon tape. The substrates are cleaned with a series of volatile solvents after dicing.

After deposition, samples are soaked in a bath of HPLC-grade water for several hours to ensure complete dissolution of salts left on the substrate from the electro spray process. Samples are dried with nitrogen, then immediately mounted in the SEM and brought under high vacuum. Samples are imaged using the same SEM. Elemental analysis is performed using a Zeiss Ultra 60 FE-SEM with an accelerating voltage of 8 keV, with energy-dispersive X-ray spectroscopy (EDX) data generated using an attached detector and software (Oxford Instruments 50 mm SDD EDX detector, Aztec 3.0 software).

3. Results and discussion

We demonstrate the formation of monolithic crystalline structures on the micron scale through a direct-write FEBID process in an unenclosed liquid film. The liquid film, which contains an aqueous salt solution, is established on the substrate in a high vacuum ($\sim 10 \mu\text{Torr}$) environment through the utilization of nanoelectrospray, delivering a charged stream of solvated precursor ions to the substrate (Fig. 1). Nanoelectrospray as a mode of liquid phase introduction for LP-FEBID benefits from significant control over liquid injection rate, dynamic control over liquid location and content, and access to non-equilibrium solution states.

The bias of the electro spray capillary has a significant influence over the behavior of deposit growth and formation, determining the overall structure (granular vs. crystalline) of the deposit, and the formation of secondary (i.e. non-beam driven) deposited material. Positive nanoelectrospray of a metal salt with elementally exclusive metal cations (e.g. silver nitrate or cupric sulfate) in solution produces an excess of secondary deposited material in the form of metal nanoparticles. Nanoparticle formation in positive mode electro spray has been previously reported [17] and is largely attributed to the rapid increase in metal cation concentration due to desolvation and droplet fission processes. In contrast, negative nanoelectrospray produces an environment with an excess of non-metallic anions and thus suppresses the formation of nanoparticles both within the electro spray droplets and within the liquid film. In addition, the presence of excess anions within the liquid bulk serves to shield metal cations from reaction with solvated electrons, limiting the rate of nucleation and growth of nanoparticles formed far from the point of beam impact.

Fig. 1 also highlights the different modes of NESA-FEBID deposit formation that occur in positive and negative electro spray modes. The excess of nanoparticle formation from positive electro spray leads to agglomeration of nanoparticles. The presence of carbon in the resulting granular deposits [7] suggests the possibility that e-beam–induced decomposition of hydrocarbons [18] plays an important role in binding the nanoparticles together. The source of the hydrocarbons that serve as a precursor for the carbon “glue” is most likely trace contamination in the sprayed liquid—concentrations of non-volatile contaminants can rapidly increase in the small films. For a typical film of thickness $\sim 2 \mu\text{m}$ and diameter 50 μm , the entire film volume is replaced every $\sim 10 \text{ms}$, and so both dissolved salt and contaminant concentrations increase rapidly.

Download English Version:

<https://daneshyari.com/en/article/8918390>

Download Persian Version:

<https://daneshyari.com/article/8918390>

[Daneshyari.com](https://daneshyari.com)