



Functional Imprinting: Post-Growth Programming of Plasmonic Domains in FEBID-based Au-C Matrices

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Additive direct-write nanomanufacturing via Focused Electron Beam Induced Deposition (FEBID) enables functional materials to be fabricated across complex substrate geometries and materials, including free-standing three-dimensional nanoarchitectures [1]. Recent advances have demonstrated that initially carbon-rich FEBID materials can be transformed into high-purity 3D gold structures in a predictable manner, linking the initially printed geometry to the final functional architecture [2,3]. Yet, functionality is typically established during growth or adapted by modifying entire structures post-growth, naturally achieving a single functionality of the 3D object. A more versatile concept would treat the as-fabricated 3D material itself as a programmable scaffold, allowing selected nanoscale regions to be converted into a second functional state after fabrication while retaining the structural and mechanical properties of the surrounding matrix.

Based on that motivation, we here establish functional imprinting in FEBID-grown Au-C metal-matrix nanostructures. Local H₂O-assisted focused electron beam irradiation selectively removes the carbonaceous matrix and converts predefined regions into nominally pure, highly crystalline Au while preserving their connection to the surrounding as-deposited scaffold. A systematic study of primary electron energies between 5 and 30 keV and H₂O partial pressures between 33 and 100 Pa reveals that lateral resolution is governed mainly by the beam diameter and backscattered-electron contributions, whereas gas pressure has only minor influence within the investigated range. The imprints reveal very high purity in the center with a gradual transition to the original Au-C chemistry. At 30 keV, total edge broadening effects range up to 38±10 nm per side, compared with 133±27 nm at 5 keV. The conversion is accompanied by a reproducible volume loss of up to 70 rel.%, which therefore becomes an intrinsic design parameter for functional imprinting.

Transferring the process to approximately 110 nm thick planar Au-C matrices yields high-purity imprints with lateral widths of below 45 nm after full optimization. Transmission Electron Microscopy (TEM) and Scanning-TEM Electron Energy Loss Spectroscopy (STEM-EELS) reveal polycrystalline Au domains with carbon levels at the detection limit, while the converted regions remain structurally integrated with the adjacent matrix. Low-loss STEM-EELS further demonstrates localized plasmonic activity: imprinted domains exhibit resonance energies and spatial mode distributions closely matching fully purified reference structures whenever the relevant modal boundaries are exposed. Modes adjacent to the lossy Au-C matrix are strongly damped, directly revealing the decisive role of the local dielectric environment.

These results shift FEBID from the direct fabrication of predefined single functional objects toward the post-growth spatial programming of functionality. Transferring this concept to three-dimensional FEBID architectures could for instance enable monolithic NEMS and MEMS elements in which the compliant mechanical behavior is governed by the carbon-rich matrix, while locally imprinted domains provide spatially defined functionality. Such domains could introduce plasmonic activity into Au-C matrices or, for example, enhanced electrical conductivity into Pt-C matrices. Functional imprinting therefore opens a route toward multifunctional 3D nanoarchitectures in which mechanical response, structural support, and locally addressable electronic or optical functionality are encoded within a single direct-write material platform.

References

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