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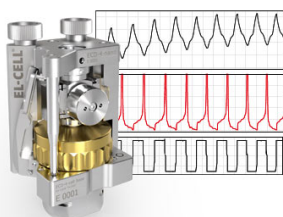
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Mapping Surface Chemistry During Superfilling with Shell-Isolated Nanoparticle Enhanced Raman Spectroscopy and X-ray Photoelectron Spectroscopy

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Silica shell-isolated Au nanoparticles are used as reporters for shell-isolated nanoparticle enhanced Raman spectroscopy (SHINERS) measurements to track and map the coverage and state of surfactant additives during electrochemical deposition. The propensity of a sub-monolayer coverage of Au@SiO_{2-x} nanoparticles to remain segregated on advancing surfaces during Cu Damascene electrodeposition is demonstrated including enrichment (dilution) on concave (convex) surface segments. The local coverage of sulfonate-terminated disulfide (SPS) and/or thiolate (MPS) accelerator and co-adsorbed chloride is mapped during superconformal deposition on SPS-derivatized trench patterned arrays. Comparison with Cu deposition on nanoparticle-free regions indicate that for sub-monolayer coverages the Au@SiO_{2-x} nanoparticles do not hinder the essential SPS/MPS adsorbate and metal deposition dynamics responsible for trench superfilling. X-ray photoelectron spectroscopy (XPS) studies on nanoparticle-free specimens reveal similar quantitative trends in SPS/MPS adsorbate coverage during metal deposition congruent with the effect of area change as detailed by the curvature enhanced accelerator mechanism (CEAC). SHINERS provides a powerful means for investigating the molecular details of superfilling and, more generally, surfactant mediated growth. © 2022 The Electrochemical Society ("ECS"). Published on behalf of ECS by IOP Publishing Limited. [DOI: 10.1149/1945-7111/ac8023]

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Additives in the form of atoms, ions and molecules are widely used as surfactants to guide morphological and microstructural evolution during electrochemical deposition of thin films. This includes both electrolytic and electroless thin film processes along with chemical reduction methods used to produce nanoparticles.^{1,2} Modern spectroelectrochemical methods have provided significant insight into the composition, structure, and dynamics of surfactant adsorbates through their optical or vibrational signatures on nominally static surfaces.³ Methods ranging from ellipsometry to surface-enhanced Raman spectroscopy (SERS) and surface-enhanced infrared spectroscopy (SEIRAS) as well as non-linear optical methods like sum frequency generation (SFG) have been applied to study surfactant-mediated growth.³⁻²⁴ Of particular interest herein is the application of these methods to study superconformal Cu Damascene electrodeposition; a process central to the metallization of microelectronic interconnects from printed circuit boards to chip stacking and on-chip wiring.^{1,4-14} However, implementation of the above methods is subject to significant limitations on specimen geometry and operating conditions, particularly with regards to *in-operando* studies where the interface is in motion. For example, many SERS studies are closely linked to the use of rough, and often unstable, plasmon active surfaces while SEIRAS measurements are usually constrained to thin IR transparent metal film electrodes that make *in-operando* studies of sustained film growth difficult.

A significant recent advance was the introduction of inert nanoparticle reporters, such as silica coated Au nanoparticles, that enable Raman spectroscopy studies on well-defined single crystal surfaces whereby the nanoparticle generates a strong electromagnetic field between the nanoparticle-substrate interface to enhance the Raman signal of molecules interacting with the surface.¹⁵ Silica, or alternative coating materials, are designed to be inert with respect to the adsorbate chemistry under study while still being thin enough to allow for effective Raman signal enhancement. The Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy (SHINERS) approach has been adopted by several researchers to examine the electrical

double layer and study molecular adsorption on well-defined single-crystal surfaces and to study reactivity as related to catalysis, batteries, electrodeposition, etc.¹⁶⁻²⁴ The present work examines the ability of such "nanoparticle reporters" to enable vibrational spectroscopy measurements during electroplating of comparatively smooth, growing surfaces under industrially relevant conditions.

The first challenge is to show that plasmonic reporter particles remain segregated, i.e., float, on moving surfaces thereby facilitating the monitoring of the coverage and conformation of surrounding adsorbates without interfering with the essential growth process under study. How the particle coverage evolves in response to the local area change induced by electrodeposition on non-planar patterned surfaces is then examined. The expectation is that the local nanoparticle coverage will respond to the area change that accompanies propagation of concave (increasing coverage) or convex (decreasing coverage) surface segments in a manner that is analogous to the conservation of floating adsorbates in the curvature enhanced adsorbate coverage (CEAC) model.^{1,25} When realized the nanoparticle reporters will enable a direct assessment of the evolving coverage of the relevant surfactant adsorbates during film growth.

Prototypical CuSO₄-H₂SO₄ superfilling electrolytes contain some combination of accelerating and suppressing additives whose competitive adsorption dynamics underlie trench and vias filling. Acceleration is usually provided by the adsorption of hydrophilic sulfonate-terminated short alkyl chain (C3) disulfide species, bis[3-sulfopropyl] disulfide (SPS) and/or mercaptopropanethiol (MPS) molecules while suppression derives from the adsorption of polyethers such as polyethylene glycol with a molar mass of 3,400 g mol⁻¹. Chloride is a necessary co-adsorbate for the above functional aspects of the accelerator and suppressor to be properly expressed. Prior work has revealed that preferential Cu deposition in trenches occurs due to enrichment of the accelerating SPS species and/or its monomer sulfonate-terminated propane thiol (MPS) on advancing concave surfaces making them more hydrophilic and thereby resistant to the adsorption of the polyether suppressor.^{1,25,26} Herein Cu deposition is examined on planar and trench patterned substrates that have been derivatized with a sub monolayer coverage of SPS, decorated with Au@SiO_{2-x} nanoparticles and electroplated in the presence of the polyether suppressor. The experiments provide direct

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observation of the enrichment of the sulfonate-terminated accelerator species on the activated concave surface segments associated with superconformal deposition. The Raman studies are further supported by X-ray photoelectron spectroscopy (XPS) measurements of planar and trench patterned specimens subject to the same derivatization and Cu deposition procedures.

Experimental

Au@SiO_{2-x} nanoparticles.—Materials.—Hydrogen tetrachloroaurate(III) hydrate (HAuCl₄•3H₂O, 99.995%), Trisodium citrate dihydrate (Na₃C₆H₅O₇, ≥99.0%), (3-Aminopropyl)trimethoxysilane (H₂N(CH₂)₃Si(OCH₃)₃, 97%) (APTMS), sodium silicate solution (Na₂O(SiO₂)_x•xH₂O, 27 wt% or 0.27 fraction by mass, *w*_{mass}), and hydrochloric acid (HCl, 0.37 *w*_{mass}, 99.999% trace metals basis) were purchased from Sigma Aldrich*. All solutions were prepared using 18.2 MΩ•cm H₂O (Barnsted). All glassware and stir bars were cleaned in aqua regia, piranha and then copious amounts of 18.2 MΩ•cm H₂O with further specifications indicated below.

Synthesis of Au@SiO_{2-x} nanoparticles.—An overview of the procedures used in the fabrication of Au@SiO_{2-x} is provided here, a more exhaustive description is provided in the supporting information (SI). Synthesis of Au particles followed Frens' method while silica (SiO_{2-x}) shell growth was built upon procedures reported by several groups.^{17,19,20,27} First, a 200 ml solution containing 0.0001 *w*_{mass} HAuCl₄•3H₂O was prepared. In a 500 ml round bottom flask the HAuCl₄ solution was heated to a boil with vigorous stirring. Once boiling, 1.4 ml of 0.01 *w*_{mass} sodium citrate was injected into the solution. Over the course of a few minutes the translucent yellow solution turned clear, then black, and then abruptly transitioned to a ruby red/purple (wine-like) color. After 30 min under boiling conditions the solution was removed from heat, to gradually cool to room temperature while stirring gently, and then filled back to 200 ml with deionized H₂O, typically ≈5 ml of H₂O had evaporated during heating. A 10 ml aliquot of the solution was transferred to a fresh 20 ml borosilicate vial with a clean microstir bar. While stirring aggressively 134 μl of a 1.5 mmol l⁻¹ (3-Aminopropyl) trimethoxysilane (APTMS) was added dropwise and the solution stirred for 20 min. Meanwhile, the silica coating media was prepared by adding 0.5 ml of 0.1 mol l⁻¹ HCl solution to 5 ml of 0.0108 *w*_{mass} sodium silicate and the resulting solution was diluted to 10 ml with deionized H₂O. A 1.1 ml aliquot of the 10 ml acidified sodium silicate solution was added dropwise to the Au-APTMS solution and stirred at room temperature for 3 min. After 3 min, the solution was submerged in a boiling water bath for 30 min, before being removed and quickly put in an ice bath. Once cooled to room temperature the Au@SiO_{2-x} nanoparticle solution was washed three times with deionized H₂O and centrifugation. After the third time the nanoparticles were concentrated between 5 to 7 times (2.2 to 1.6 ml total volume) for immediate use in SHINERS measurements. Tests of Raman enhancement and shell efficacy of the Au@SiO_{2-x} nanoparticles are detailed in the SI.

Cu electrodeposition experiments.—The electrolyte was comprised of 1.8 mol l⁻¹ H₂SO₄, 0.24 mol l⁻¹ CuSO₄•5H₂O, 1 mmol l⁻¹ NaCl, and 88 μmol l⁻¹ polyethylene glycol (PEG, average molar mass ≈ 3,400 g mol⁻¹) where the polymer was added to the base electrolyte at room temperature. A three-electrode cell was utilized for all measurements where the Cu counter electrode compartment was separated from the working electrode compartment by a Nafion 417 proton exchange membrane. The Hg/Hg₂SO₄ reference electrode was placed laterally adjacent to the working electrode to minimize the distortion of the current path to the counter electrode. The same electrode positioning was maintained between experiments to minimize variation in the ohmic iR drop. Planar specimens for Raman and XPS studies were fabricated by physical vapor evaporation of 100 nm Cu on a Ti seeded Si(100) wafer. Feature filling experiments were performed on trench patterned wafers

(Q-cleave D Reticle from Semitech/ADTF/Skorpios Technologies) that were covered with Ta barrier layer and seeded with a thin sputtered Cu layer. The sputtered and physical vapor deposited (PVD) films are expected to have a (111) texture along the surface normal. For the majority of experiments the Cu seeded wafer fragments (generally 2 cm × 1 cm) were derivatized for 30 s in 0.1 mol l⁻¹ H₂SO₄ containing 50 μmol l⁻¹ bis[3-sulfopropyl] disulfide (SPS) and then rinsed by a 3 s to 4 s dip in H₂ saturated 4 μmol l⁻¹ HCl solution then dried with an Ar jet. Immediately thereafter, 2 μl portions of the concentrated (7.7 × 10¹⁰ Au@SiO_{2-x} nanoparticles/ml) Au@SiO_{2-x} solution were dropcast onto the patterned wafer, and the wafers were dried in a chamber under a gentle flow of Ar gas. The hydrophilic surface proved to be ideal for the formation of an evenly distributed sub-monolayer Au@SiO_{2-x} nanoparticle film. The freshly prepared Au@SiO_{2-x} decorated Cu seeded wafer fragments were immersed into the electroplating bath under potential control at -0.625 V vs Hg/Hg₂SO₄ and held for 60 s, 120 s or 180 s of Cu deposition and then, rinsed in H₂ saturated 4 μmol l⁻¹ HCl, and dried in an Ar flow followed by immediate transfer, under inert conditions, into either an Ar fed Raman cell or XPS spectrometer.

Characterization.—After Au@SiO_{2-x} nanoparticle dropcasting and Cu deposition, both the growth front and distribution of Au@SiO_{2-x} nanoparticles on the free surface and cross-section were examined using a FEI Quanta scanning electron microscope (SEM). Energy Dispersive Spectroscopy (EDS) maps were generated using a Bruker Quantax at 20 kV. For cross sections, the specimens were embedded in epoxy and then sectioned perpendicular to the trench length followed by mechanical polishing to 0.05 μm-grade diamond finish and ion polishing in a Gatan ion mill. Transmission electron microscopy (TEM) images of the Au@SiO_{2-x} nanoparticles were acquired on a 300 kV FEI Titan. UV-vis measurements were taken using a Cary 4000 UV-vis spectrometer. XPS measurements were performed using a Kratos Analytical AXIS Ultra DLD spectrometer. The analysis chamber of the spectrometer typically maintained an ultra-high vacuum (UHV) working pressure below 3.6E-7 Pa during the measurements. Freshly immersed and rinsed specimens were transferred to the spectrometer under an Ar atmosphere and subject to analysis without further treatment. Spectra were collected using a monochromatic Al Kα X-ray source with a 20 eV analyzer pass energy and a 0.7 mm × 0.3 mm spot size. Spectra were evaluated using Casa XPS software and further quantitative analysis is detailed in the SI.

Raman measurements.—All Raman spectra were acquired using a Renishaw InVia microscope spectrometer, with 633 nm He-Ne laser excitation source, in backscattering configuration with a 50× objective (N.A. = 0.75, spot size ca. 1 μm to 2 μm), 1800 lines mm⁻¹ grating and 2.54 cm charge-coupled device detector (1024 × 256 channels). Rectangular Raman maps were collected, under continuous Ar flow using a Raman flow cell, with step sizes of 2 μm in a ≈10 by 38 rastered grid. Each point was acquired for 3 s. The Ar flow cell was built using 0.3175 cm thick polyether ether ketone (PEEK) with a quartz coverslip window over the enclosed wafer segment. Following derivatization and Cu electroplating the specimen (≈2 cm × ≈1 cm) was assembled in the Raman cell and transferred, in a larger Ar flooded container, to the Renishaw spectrometer where an Ar gas purge line was connected to the cell to enable an O₂ free atmosphere to be maintained during the measurements minimizing oxidation of the Cu surface. Prior to all experiments the spectrometer was calibrated using a Si standard.

Feature filling simulations.—Simulations predicting Cu feature filling and SPS surface coverage are based on the curvature enhanced accelerator coverage (CEAC) mechanism.¹ The full system of equations outlined in Ref. 1 is solved numerically in a 2D geometric configuration with the COMSOL Multiphysics version 5.6 software package implementing the following modules: tertiary

current distribution, surface reaction, and deformed geometry. The default solver was used with 2D triangular mesh elements having a minimum refined size of 5 nm along each side near the electrode interface, scaling as large as 750 nm per side at a distance greater than 13 μm from the workpiece surface. Automatic remeshing is enabled, occurring when the maximum mesh distortion parameter exceeds 0.5. A moving boundary smoothing parameter of 1, geometric shape order of 1, and hyperelastic mesh smoothing type are used in the deformed geometry module (see COMSOL documentation for a detailed explanation on how these parameters impact moving boundary convergence). Meshing was refined such that the system of equations is solved with an overall charge imbalance (the fractional difference between the total integrated currents at the counter and working electrode) is less than 0.2%. To give a sense of the computational expense, typical simulations with an aspect ratio of 2, having 8500 domain elements and 750 boundary elements mesh elements, took on the order of tens of minutes to compute on a Dell Precision 3630 desktop computer with an Intel Xeon E-218G CPU @ 3.80 GHz and 64 GB RAM using Windows 10 Enterprise 64-bit operating system.

Results and Discussion

Synthesis of Au@SiO_{2-x} reporters.—The concepts behind silica encapsulation of metallic nanomaterials have been previously explored, although some important aspects were only lightly discussed.^{16–18,22} Five elements are essential for successful production of silica coated Au nanoparticle reporters (Fig. 1a). First, cleanliness of the initial Au nanoparticle synthesis, treating all glassware, stir bars, etc with nitric acid and then boiling in 18.2 MΩ. cm H₂O, prevented aggregation of as-formed Au nanoparticles. Second, introduction of (3-amino-propyl) triethoxysilane (APTMS) linker solution to the Au nanoparticle solution must be done very slowly (one drop at a time) with rapid stirring otherwise aggregation will occur. Third, when preparing the silicate solution, the amount of acid added should be precise and added dropwise to mitigate excess free silica formation. During shell growth stable reaction temperature is essential for reproducible shell growth rates, so the surrounding water reservoir was fixed at the boiling point as opposed to 90 °C often reported in literature.^{15–18,22} Finally, as hinted to above, there is a striking dependence between the amount of acid added during preparation of the initial silicate solution as both the SiO_{2-x} shell growth rate and final thickness (Figs. S1–S2 (available online at stacks.iop.org/JES/169/082506/mmedia)) are highly sensitive to pH. During the silica coating process once the equilibrium pH, near 10.35 (measured at room temperature), is reached little to no further shell growth occurs thus providing a helpful end point.²⁸ Following synthesis, the reporters were sized at 72 nm with a standard deviation of ± 13 nm for the Au core and $2.3 \text{ nm} \pm 0.2 \text{ nm}$ for the silica shell by TEM (Figs. 1a, S3). UV–vis absorption measurements confirmed the expected 534 nm absorption peak for fully dispersed and solvated core–shell Au@SiO_{2-x} particles (Fig. S4). To ensure Raman enhancement of the Au@SiO_{2-x} reporters, in the absence of silica shell pinholes, voltammetry of Au@SiO_{2-x} nanoparticles on glassy carbon probed for Au redox peaks while pyridine was used as a probe molecule for open Au surface sites.^{15–18} (Fig. S5). Voltammetry in 10 mmol l⁻¹ KOH using bare Au nanoparticles demonstrated redox peaks between 0.1 V to 0.5 V vs Hg/HgO that are absent in the case of Au@SiO_{2-x} reporters (Fig. S5a). In another experiment the absence of pyridine adsorption was used to confirm the absence of pinholes, an observation that was also supported by the absence of aggregation in Au@SiO_{2-x} relative to Au nanoparticles (Fig. S5b, inset) and the lack of a Raman signal when the Au@SiO_{2-x} nanoparticles, supported on Si, were covered with a drop of 10 mmol l⁻¹ pyridine solution (Fig. S5b). When the Si substrate was replaced with a 100 nm evaporated Au film (Fig. S5b) vibrational enhancement of pyridine absorbed on the planar Au surface by the overlying Au@SiO_{2-x} nanoparticles was evident.

Surface segregation of Au@SiO_{2-x} reporters during Cu electrodeposition for planar surfaces.—For SHINERS to accurately report on the conditions at an actively growing electrodeposited surface requires the particles remain surface segregated and thence effectively float upon the advancing interface (Fig. 1b). This is demonstrated by comparing surface regions and cross-sections of the electrodeposits grown in the presence of dropcast particles (Figs. 1c–1e) on a bis-(3-sulfopropyl) disulfide (SPS)-derivatized surface. Attention was focused on regions where the dropcast Au@SiO_{2-x} nanoparticles coverage is in the sub-monolayer regime like that shown in Fig. 1c. Following 1 min and 3 min of potentiostatic Cu deposition in 0.25 mol l⁻¹ CuSO₄–1.8 mol l⁻¹ H₂SO₄–1 mmol l⁻¹ NaCl–88 $\mu\text{mol l}^{-1}$ PEG at $-0.625 V_{\text{SSE}}$ the deposit surface (Fig. 1d) and cross-section (Fig. 1e) were examined by SEM. It is evident that all the Au@SiO_{2-x} nanoparticles remain segregated or float upon the growing surface (Fig. 1e) during Cu electrodeposition, at a rate of $\approx 0.4 \mu\text{m min}^{-1}$, in the presence of the accelerating SPS surfactant additive.

Raman spectroscopy was performed on both freshly derivatized and electrodeposited specimens. For reference purposes, the SPS-derivatized Cu thin film (Fig. 1f) was examined first. Spectra in Fig. 1f are presented post-subtraction of a broad spectral background, narrower windows were used for integration purposes. Spectra collected from a pristine Au surface with and without Au@SiO_{2-x} nanoparticles (Fig. S6) reveal that the background originates from the Au@SiO_{2-x} nanoparticles themselves. The spectrum for the derivatized Cu (111) textured thin film seed layer reveals the characteristic peaks for adsorbed Cl⁻ at 300 cm⁻¹, i.e. $\nu(\text{Cu-Cl})$, followed by a quartet of peaks, assigned to *Gauche* $\nu(\text{CS}_{\text{RS}})$, *Trans* $\nu(\text{CS}_{\text{RS}})$, $\rho(\text{CH}_2)/\tau(\text{HCCC})$, $\nu(\text{CS}_{\text{RSO}_3^-})$ between 600 cm⁻¹ and 800 cm⁻¹ for SPS and likewise the symmetric SO₃⁻ stretch, $\nu_s(\text{S=O})_{\text{RSO}_3^-}$, at 1036 cm⁻¹; $\nu_s(\text{S=O})_{\text{RSO}_3^-}$ and $\nu(\text{Cu-Cl})$ will henceforth be abbreviated to ν_{RSO} and ν_{CuCl} . Among the SPS-related quartet, between 600 cm⁻¹ to 850 cm⁻¹, possible overlap with Cu surface oxidation, $\nu(\text{Cu}_2\text{O})_{\text{surf}}$ at 627 cm⁻¹, needs to be considered (see 1 min in Fig. 1f). It should be noted that several of the mode assignments for the disulfide SPS overlap those of the monomer thiol MPS (see reference spectra, Figs. S7–8, Table I and Tables SIII–SIV) so no attempt is made to distinguish between these two molecules at this juncture. The peak at 976 cm⁻¹ is ascribed to residual sulfate, $\nu(\text{S=O})_{\text{H}_2\text{SO}_4}$, from the electrolyte that remains following the immersion and rinsing process, although possible contributions from oxidation of the adsorbed SPS/MPS molecules cannot be ruled out. Reference spectra (Figs. S7–S8) for fully solvated molecular additives SPS, MPS, and PEG also reveal a series of CH alkane modes at higher wavenumbers, 1200 cm⁻¹ and 1500 cm⁻¹, followed by the envelope for the methylene stretches between 2800 cm⁻¹ and 3000 cm⁻¹, the latter to be revisited below. Select vibrational mode assignments for these peaks based on literature references is provided in Table I with a more extensive list located in the SI (Tables SIII–SIV).

Following 1 min and 3 min of Cu electrodeposition on the SPS-derivatized surface the symmetric SO₃⁻ stretch at 1036 cm⁻¹ and neighboring quartet of thiol-propane-sulfonate related modes between 600 cm⁻¹ and 850 cm⁻¹ (Fig. 1f) are still present indicating that, like the Au@SiO_{2-x} nanoparticles, substantial coverage of the SPS/MPS accelerator species remain confined to the growing surface even after 3 min of Cu electrodeposition. Nevertheless, a significant and rapid decrease in SPS/MPS coverage occurs during the first increment of metal deposition on the derivatized electrode. This is congruent with the surfactant quality of the SPS/MPS being dependent on the co-adsorption of a high coverage of chloride that hinders sulfidation of the Cu.³³ Chloride is the dominant additive in the electroplating electrolyte, rapidly adsorbing on available surface sites and readily displacing adsorbed SO₄²⁻ under these conditions.^{1,33} The magnitude of the ν_{CuCl} mode at 300 cm⁻¹ is used as an internal reference to quantify the evolution of the SPS/MPS accelerator species. This also serves as an avenue for normalizing variations in Raman enhancement with particle

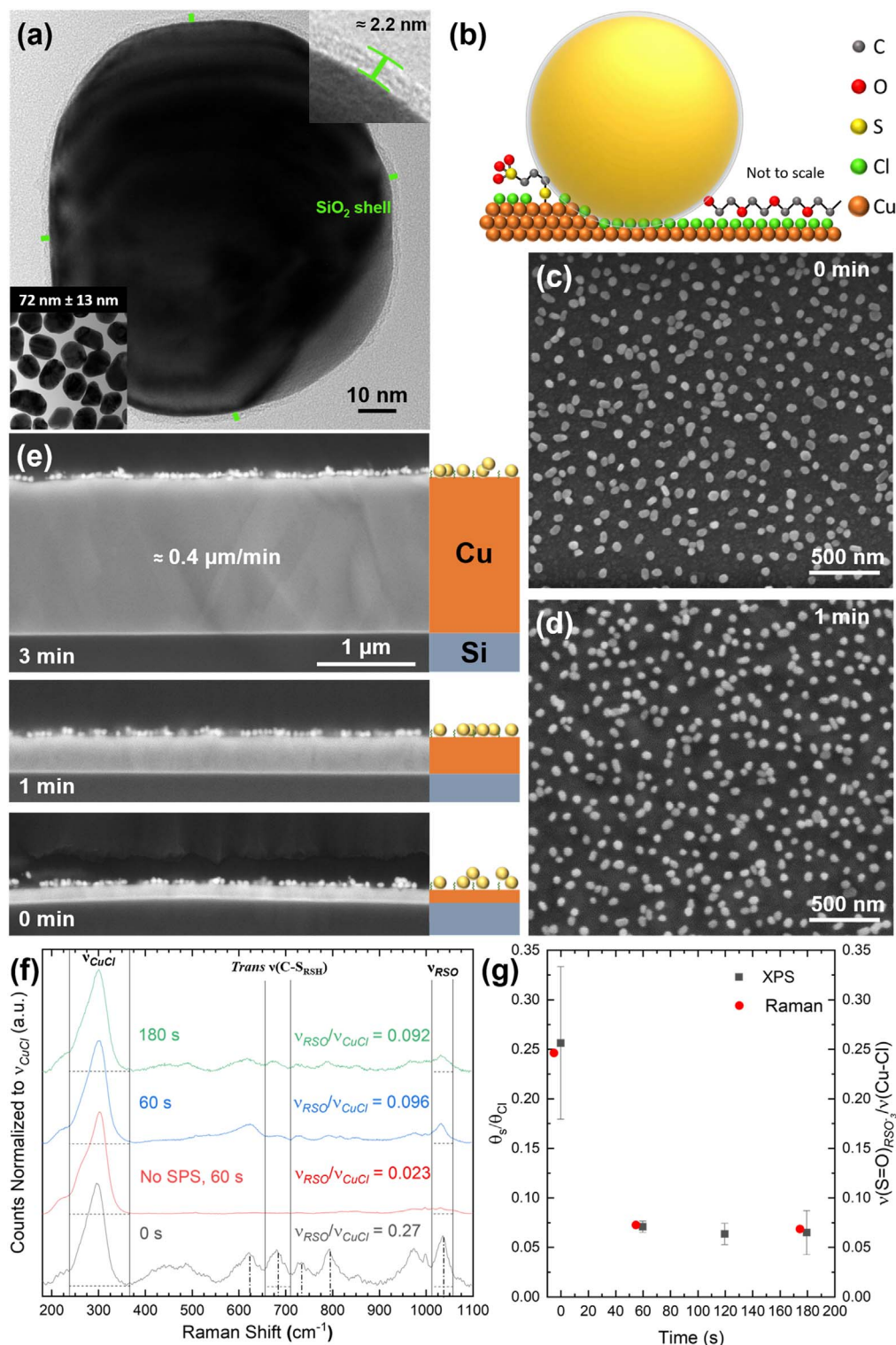


Figure 1. (a) 72 nm Au nanoparticles with a 2.3 nm SiO_{2-x} shell were dropcast onto a Cu thin film for (b) SHINERS measurements. SEM images of dropcast Au@SiO_{2-x} nanoparticles on a SPS-derivatized Cu thin film (c) before and (d) after 1 min of Cu electrodeposition showing the Au@SiO_{2-x} remain segregated, i.e. float, on the advancing metal-electrolyte interface. (e) Cross-sections after Au@SiO_{2-x} drop casting followed by 1 min and 3 min of Cu deposition. (f) Raman spectroscopy, using a 633 nm laser, reveals the sulfonate-terminated thiol/disulfide accelerator on the derivatized electrode remains co-adsorbed with Cl⁻ on the advancing Cu surface where the spectra are scaled to the intensity of 300 cm⁻¹ $\nu(\text{Cu-Cl})$ band. The vertical solid lines connected with dashed lines in (f) indicate the regions integrated for the notated peaks. (g) Comparison of the sulfur, "thiolate" vs chloride ratio from XPS to the $\nu(\text{S=O})_{\text{RSO}_3^-}$ vs $\nu(\text{Cu-Cl})$ ratio from SHINERS. The position of the SHINERS ratios in (g) have been shifted by -3 s for visual clarity.

density. Taking the empirical ratio of the integrated peak area for the 1036 cm⁻¹ ν_{RSO} to the 300 cm⁻¹ $\nu_{\text{Cu-Cl}}$ Raman modes, ($\nu_{\text{RSO}}/\nu_{\text{Cu-Cl}}$), reveals a drop from 0.27 to 0.096 within the first minute of metal

deposition while a much smaller decrease to 0.092 occurs following 3 min of Cu deposition. Raman after 1 min of electrodeposition in the absence of SPS demonstrates a few minor peaks, possibly affiliated with

Table I. Vibrational mode assignments to spectral peaks observed via Raman measurements. A more extensive list is provided in the supporting information (Tables SIII and SIV).

Raman Shift (cm ⁻¹)	Assignment	References
300	$\nu(\text{Cu-Cl})$	7, 29,30
509	$\nu(\text{SS})$	7
528	$\nu(\text{Cu}_2\text{O})_{\text{surf}}$	31
624	<i>Gauche</i> $\nu(\text{C-S}_{\text{RS}})$	7,19
627	$\nu(\text{Cu}_2\text{O})_{\text{surf}}$	31
686	<i>Trans</i> $\nu(\text{C-S}_{\text{RS}})$	7, 19,23
727	$\rho(\text{CH}_2)$, $\tau(\text{HCCC})$	19
791	$\nu(\text{CS}_{\text{RSO}_3-})$	19
976	$\nu_s(\text{S=O})_{\text{H}_2\text{SO}_4}$	19, 31,32
1033	$\nu_s(\text{S=O})_{\text{RSO}_3-}$	7
2927	$\nu_s(\text{CH}_2)_{\text{solv}}$	5
2944	$\nu_a(\text{CH}_2)$	5

ν , stretch; δ , bend/scissor; τ , twist; ρ , rock; a , asymmetric; s , symmetric

polyether modes, that make a relatively broad background overlapping with 1036 cm⁻¹ (ν_{RSO}) (Fig. 1g).⁷ The area associated with this background (0.023) was subtracted (e.g. 0.096–0.023 and 0.092–0.023 for 1 min and 3 min, respectively) from the Raman peak ratio summarized in Fig. 1g and related discussions.

Similar experiments with Au@SiO_{2-x} nanoparticle-free planar specimens subject to the same SPS/MPS derivatization and Cu electroplating treatments were examined by XPS; representative survey and core-level spectra are shown in the supplement, Figs. S9–S12. The S 2p spectra for the as derivatized SPS surface is fit assuming a one-to-one area ratio between the low energy 2p_{3/2} (and 2p_{1/2}) thiolate-related peaks, 162.3–162.5 eV, and the sulfonate peaks, 167.85 eV, while the remaining intensity is ascribed to sulfate, 168.66 eV, associated with residual electrolyte from the emersion process (Fig. S10a). Closer inspection also reveals the presence of a less intense, lower binding energy sulfide state as shown in Fig. S10e. A well-resolved Cl 2p spin-orbit doublet peak is evident near 198.2 eV (Fig. S10b) along with the Cu 2p_{3/2}, 832.65 eV, L₃M_{4,5}M_{4,5} Auger line, 568.0 eV, and Cu 2p_{3/2}-Cu L₃M_{4,5}M_{4,5} Auger parameter, 1851.39 eV that collectively indicate the derivatized Cu electrode is largely in the elemental state with adsorbed Cl⁻ and thiolate being distinct from bulk compounds such as Cu₂S, CuCl, CuCl₂, Cu₂O, CuO or CuSO₄ (Fig. S10c).³⁴

For reference purposes, the surface of an SPS-free electrode was examined following 1 min of Cu electrodeposition at -0.625 V in 0.25 mol l⁻¹ CuSO₄ – 1.8 mol l⁻¹ H₂SO₄ – 1 mmol l⁻¹ NaCl – 88 μ mol l⁻¹ PEG. As shown in Fig. S11, the Cl 2p and Auger parameter indicate that the Cu surface is covered with a halide adlayer while the C 1s peak at 286.5 eV and associated O 1s component (not shown) reveal the presence of the PEG overlayer, Fig. S11d, that suppresses the metal deposition reaction. The S 2p spectrum of the emersed electrode exhibits a significant sulfate signal that might be related to residual electrolyte although, in contradiction, no corresponding increase in the Cu²⁺ shake up is evident in the Cu 2p or Auger spectrum (Fig. S11c).³⁴

Next, the surface of the SPS-derivatized electrodes were examined following Cu deposition at -0.625 V in 0.25 mol l⁻¹ CuSO₄ – 1.8 mol l⁻¹ H₂SO₄ – 1 mmol l⁻¹ NaCl – 88 μ mol l⁻¹ PEG. Representative XPS S 2p and Cl 2p spectra, Figs. S12a–S12b, reflect adsorbed thiolate and chloride and the Cu 2p_{3/2}-Cu L₃M_{4,5}M_{4,5} Auger parameter, Fig. S12c, confirms the metallic nature of the electrodeposited Cu surface. The absence of unbound disulfide indicates that any physisorbed or weakly adsorbed SPS has been rinsed away or perhaps oxidized during the emersion process.³⁵ Relative to suppressed deposition on the SPS accelerator-free surface, the C(1 s) (Fig. S12d) reveals a decrease in the magnitude of the inhibiting polyether C(1 s) peak at 286.5 eV due to the repulsive interaction induced by the hydrophilic sulfonate end group

of the adsorbed SPS/MPS accelerator. Going further, assuming a one-to-one correspondence between the low binding energy thiolate and disulfide head-group, and the sulfonate end-group, a simple overlayer model can be used to estimate the fractional surface coverage of chloride, θ_{Cl} , and the thiolate and/or related low binding energy S species, θ_{S} . Seah's³⁶ most recent universal expression for electron attenuation lengths is used in combination with Kratos sensitivity factors, transmission function, and angular corrections to yield an estimate of the fractional coverage, θ_{S} and θ_{Cl} , on both the derivatized and electroplated specimens. Further details on the overlayer model are presented in the supporting information section “XPS Quantification.” Absent comparable knowledge of the Raman scattering cross-section for ν_{CuCl} vs ν_{RSO} , surprisingly good agreement is evident between the $\nu_{\text{RSO}}/\nu_{\text{CuCl}}$ ratio and the surface coverage ratio, $\theta_{\text{S}}/\theta_{\text{Cl}}$, determined by XPS as shown in Fig. 1g.

Significant dispersion in the thiolate and chloride coverage was observed between different derivatized specimens. This is primarily due to variations in the halide levels in the nominally “Cl-free” SPS derivatization solutions over six independent experimental series. Lower Cl⁻ concentrations lead to higher thiolate/halide ratios on the derivatized electrodes. Despite the initial variations in the $\theta_{\text{S}}/\theta_{\text{Cl}}$ ratio of the derivatized surfaces, the coverage on the electroplated surface quickly focuses to a narrower range of values as evident in Figs. 1g and S13. This is consistent with a high halide coverage being important to the ability of the SPS/MPS to float on the surface during Cu deposition congruent with earlier observations.^{26,33}

Across the planar series the halide coverage following electrodeposition varied between $0.42 < \theta_{\text{Cl}} < 0.52$ against the density of metallic Cu while the thiolate coverage ranged between $0.017 < \theta_{\text{S}} < 0.041$. The halide coverage is congruent with that reported for saturated Cl adlayer surface structures on the three primary surfaces, Cu (111) $\theta_{\text{Cl}} = 0.39$, Cu (100) $\theta_{\text{Cl}} = 0.5$, and Cu (110) $\theta_{\text{Cl}} = 0.66$, giving an average of $\theta_{\text{Cl}} \approx 0.5$ based on the variations in metal density between the different surfaces. The much smaller “thiolate” coverage on the actively plated surface compares well with the $\theta_{\text{S}} \approx 0.02$ lower bound seen by in situ STM studies of the near steady-state coverage following extended SPS interaction with the c(2x2) Cl saturated Cu (100) in 30 μ mol l⁻¹ SPS – 0.001 mol l⁻¹ HCl – 0.1 mol l⁻¹ HClO₄ solution at potentials similar to that used in the present experiment.³³

The θ_{S} evolution of the SPS-derivatized electrodes with Cu deposition can also be compared with predictions based on the curvature enhanced coverage model.^{1,25,26} In prior work the fractional SPS coverage on an actively growing electrode, that had been derivatized for 30 s in 50 μ mol l⁻¹ SPS in 1.8 mol l⁻¹ H₂SO₄, was estimated to be 0.054 of saturation based on $\Gamma_{\text{SPS}} = 6.35 \times 10^{-10}$ mol SPS cm⁻².¹ Instead, in the present work, the measured thiolate coverage is referenced to the underlying metal lattice, i.e. Cu (100) = 2.54×10^{-9} mol cm⁻². Adjusting for the monomer character of thiolate and different saturated reference state yields an equivalent thiolate coverage of $\theta_{\text{S}} \approx 0.027$. Using kinetics for Cu deposition and SPS consumption determined from prior electro-analytical and XPS studies the modest deactivation for derivatized electrodes with a starting coverage of $\theta_{\text{S}} \approx 0.025$ and 0.05 are compared to the measured values in Fig. 8d, vide infra.¹ These exact values are, of course, subject to the background selected in the XPS analysis but regardless of such variations favorable comparison with the modest deactivation trend remains.

The experiment with planar electrodes demonstrates that the Au@SiO_{2-x} reporters “float” on planar surfaces during electrodeposition and enable Raman measurements of the sub monolayer coverage of Cl⁻ and SPS/MPS derived accelerator species in good agreement with parallel ex situ XPS measurements of the respective surface species following Cu electrodeposition in the absence of Au@SiO_{2-x} nanoparticles.

Trench arrays: influence of area change on Au@SiO_{2-x} nanoparticle density.—The propensity of “floating” Au@SiO_{2-x} nanoparticles to be conserved during area change that accompanies

Cu deposition on non-planar surfaces was explored using 500 nm deep patterned trench arrays. Following derivatization in $50 \mu\text{mol l}^{-1}$ SPS – 0.1 mol l^{-1} H_2SO_4 for 30 s and dropcasting Au@SiO_{2-x} nanoparticles, Cu was electrodeposited on the trench arrays for the specified duration and subject to Raman spectroscopy and subsequent examination of the trench surface and cross-section by SEM. As a control measure, a subset of specimens without Au@SiO_{2-x} nanoparticles were subject to a parallel metallurgical study. Six different trench widths were examined where the wall width between trenches was 250 nm, Fig. S14. The individual arrays are specified by the trench width and wall width, e.g. the 1:5 trench array corresponds to $1.25 \mu\text{m}$ wide trenches that are 5 times longer than the 250 nm wide walls separating individual trenches, Fig. S14 (blue highlight).

Following 1 min of Cu electrodeposition the Au@SiO_{2-x} reporters remain segregated on the growth front, Fig. 2, like that seen in planar deposition experiments. Close inspection reveals that the local reporter coverage increased along the bottom corners. The enrichment being a direct consequence of the area reduction that accompanies conversion of the original right-angled corners to the propagated triangulated profile. With further deposition, the nanoparticles remain segregated on the growing surface as the trench arrays are overfilled with Cu by 3 min. The Au@SiO_{2-x} reporters, originally distributed evenly along the substrate profile, are now concentrated along the centerline of the trench overburden, Fig. 2c. The substantial overburden that has developed above the trenches arises from area change driven enrichment of the accelerator during the filling process as detailed by the CEAC shape change model.¹ In an identical fashion, the elevated density of Au@SiO_{2-x} nanoparticles on surface segments that experienced superconformal film growth also reflect the impact of area change. The rearrangement and evolution of the Au@SiO_{2-x} nanoparticles coverage with Cu deposition in the trench array can also be monitored *via* energy dispersive spectroscopy (EDS) SEM mapping, Fig. S15. For the as-

dropcast specimen, Fig. S15a, the higher $\text{Au } M_{\alpha,\beta}$ signal at the edges of the trench walls, and corresponding decreased Cu K_{α} signal, in the 2-D map rendering reflects the summed coverage of the uniformly distributed Au@SiO_{2-x} on the sidewall of the trenches. Following 1 min of Cu electrodeposition, Fig. S15b, the dominant Au signal is displaced inwards toward the trench middle forming two bands of Au@SiO_{2-x} particles enriched on the advancing triangular trench corners.

After 3 min of Cu deposition, Fig. S15c, further propagation of the concave growth front leads to the highest Au signal being aligned with the centerline of the filled trench. The organization and local enrichment of the Au@SiO_{2-x} nanoparticles mimics, and is a direct consequence of, the SPS accelerator driven shape change of the growth front. For these conditions, the mass balance principle of surfactant adsorbate conservation also applies to the Au@SiO_{2-x} nanoparticle reporters. The redistribution of nanoparticle reporters with area change provides an almost ideal configuration for the selective Raman spectroscopy study of the surface chemistry associated with regions of accelerated deposition. Further still, as Raman enhancement is related to plasmonic coupling between adjacent nanoparticles,³⁷ close tuning of the initial reporter coverage against the anticipated area reduction should enable optimization of the Raman signal from the most actively growing region of a given specimen.

Simulations based on the curvature enhanced accelerator coverage model (Figs. 2d–2f) are presented for Cu deposition on the same trench array geometry.^{1,38} The surface was derivatized to establish a uniform fractional SPS coverage of $\theta_s = 0.05$. The derivatized surfaces were then subject to 1 min and 3 min of Cu electrodeposition. Simulation results for 1 min of deposition (Fig. 2e) are in excellent agreement with the experimental filling profile showing the corners experience a significant increase in accelerator coverage to a fractional coverage of ≈ 0.121 . For 3 min of deposition (Fig. 2f) the simulations capture the overfilled growth

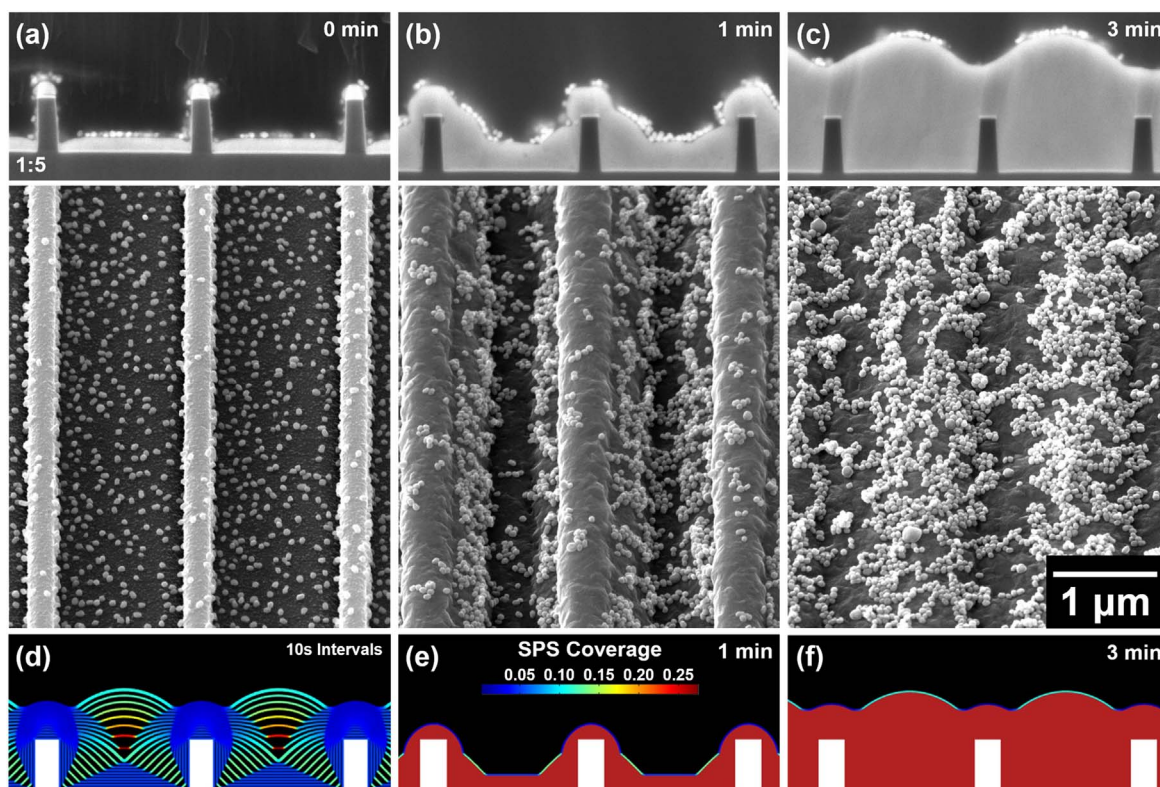


Figure 2. Cross-sections and perspective (tilted 45° away from surface normal) images of trench filling and Au@SiO_{2-x} nanoparticles coverage evolution after (a) 0 min (b) 1 min and (c) 3 min of Cu electrodeposition. Simulations of feature filling electrodeposition with (d) contours of the growth front every 10 s colored to reflect the SPS/MPS accelerator coverage (e) Growth front of partially filled trench after 1 min of deposition and (f) the over filled trench after 3 min of deposition. Accelerator coverage contours in (d)–(f) are specified by the colorized scale bar in (e).

front geometry. Inspection of the growth contours, Fig. 2d, reveal the highest coverage of accelerator ≈ 0.275 , is reached at the center of the trench just prior to inversion of curvature at ≈ 2 min, after which the local surface concentration of accelerator begins to decrease as the interface area begins to dilate to reach a final coverage of ≈ 0.105 by 3 min.

Trends between trench arrays with different widths.—Similar trends were evident for the trench arrays with different aspect ratios in Fig. S14 (orange highlight). In a typical experiment Au@SiO_{2-x} nanoparticles were dropcast over the entire recessed patterned region (Fig. 3a). The well-defined perimeter of the recessed trench patterned region of interest (Fig. S14) served to guide droplet wetting to yield favorable reproducibility and reasonably uniform particle distribution between drop-casts over the six trench arrays as determined by visual and SEM examination (Fig. 3a). The six arrays shown are separated by 2.5 μm wide recessed flats (Fig. S14a). Each array has eight trenches that are 500 nm deep and separated by 250 nm wide walls. Cross-section images and 45° perspective SEM images (Fig. 3a) show that the initial Au@SiO_{2-x} nanoparticle distribution is reasonably uniform across the arrays while EDS Au-M _{$\alpha\beta$} mapping measurements provide another means to map the nanoparticle coverage and distribution across the trench arrays (Figs. 4 and S16). For the derivatized specimen, Fig. 4a, each trench array has nine peaks in Au signal corresponding to the nine trench walls and the summed coverage of Au@SiO_{2-x} thereon. The eight valleys between the Au M _{$\alpha\beta$} signal peaks reflect the coverage of particles on the trench bottom. Deviations are evident for the smaller features where convolution of the measurement with screening by sidewalls of the higher aspect ratio trenches exerts an increasingly important role. Nevertheless, the similar intensity profile for the Au M _{$\alpha\beta$} maps between the 1:10 and 1:1.5 trench arrays is congruent with the imaged particle density and reflects the degree of uniformity in particle distribution across the freshly derivatized work piece that can be realized by dropcasting.

Following 1 min of Cu electrodeposition (Fig. 3b), (on a substrate prepared in parallel with that shown in Fig. 3a) significant deposition has occurred from the trench corners of the 1:10, 1:5, 1:3 and 1:2 trench arrays with the bottom surface slightly more advanced for smaller trench widths. For the 1:1.5 trenches the superconformal growth front has just emerged from the trench while the highest density trench array, 1:1, are nominally filled although several Au@SiO_{2-x} particles have been trapped within the trench with the cusp shape of the emerging growth front indicative of marginal superfilling at best. The trapped and agglomerated Au@SiO_{2-x} particles within the 1:1 trenches (Fig. 3b) are in contact with the trench sidewall, suggestive of defects in the seed layer due to either poor step coverage of the sputtered Cu seed layer and/or corrosion from extended aging of the wafers in the laboratory ambient. It is likely the particle(s) in contact with the sidewall defects serve as competing centers for aggregation of particles at the advancing growth front. For all other trench arrays the enrichment of the Au@SiO_{2-x} nanoparticles within the recessed concave regions demonstrates the ability of the nanoparticles to float on the advancing surface undergoing area reduction during superconformal growth. Likewise, the inverse, dilution of particles occurs on the more slowly advancing convex upper wall surfaces between individual trenches. EDS maps of the Au M _{$\alpha\beta$} also reveal (Fig. 4b, S15, S16) the reorganization of the Au@SiO_{2-x} nanoparticles with area change. Compared to the dropcast sample, Fig. 4a, the average Au M _{$\alpha\beta$} signal increases monotonically as the trench aspect ratio increases from 1:10 to 1:1.5 (Fig. S17a). For the highest aspect 1:1 trench array the sharp decrease in Au M _{$\alpha\beta$} intensity below that of the other trench arrays is consistent with Au@SiO_{2-x} being trapped in the upper half of the narrowest trenches. For the lowest aspect ratio 1:10 array the nine Au M _{$\alpha\beta$} EDS peaks seen prior to deposition are split into two (e.g. nine sets of two peaks) reflecting the enrichment and migration of Au@SiO_{2-x} particles associated with propagating trench corners. The same observation applies to the

1:5 array, Fig. S15, while for the 1:3, 1:2 and 1:1.5 trench arrays, Fig. S16, the two advance corners have or are about to merge and the intensity of the Au M _{$\alpha\beta$} at the center of the trench has now increased well above that of the original dropcast surface (Figs. S17b, S17c). This is confirmed by the fact that there are now ten Au M _{$\alpha\beta$} peaks, eight corresponding to the enriched particles along the centerline of the eight trench bottoms flanked on either side by peaks relating to the enrichment on the outer corners of the trench array that face the 2.5 μm wide recessed gap between the arrays, Figs. 4b and S16. The same trends are also evident in the SEM cross-sections and perspective images in Fig. 3 for the 1:3, 1:2 and 1:1.5 arrays where the enriched particles form into clusters extended along the trench center line.

CEAC simulations of trench filling during Cu deposition show the strong dependence of the filling profile on area change, Figs. 2 and 5. The growth profile on flat surface segments is conformal while the impact of area change on accelerator coverage and accelerated growth at the trench corners is evident. Further differentiation follows as the growth front from opposing trench corners begin to interact and the rate of area reduction and accelerator enrichment increase sharply. After 1 min of simulated deposition (Fig. 5a) the first stage of accelerator enrichment at the individual trench corners is evident for the 1:10 and 1:5 arrays. For the 1:3 array the corners are on the verge of interacting while for the 1:2 and 1:1.5 arrays the transition to accelerated bottom-up filling is well underway. The simulated growth front for the 1:1.5 array is slightly more advanced than in the experiment while for the 1:1 array the simulated bottom-up growth front has managed to escape the trench. In contrast, the experimental results for the 1:1 array yielded a void that is at least partly the result of the overhanging seed layer that effectively increased the aspect ratio of the trench. The surface coverage, θ_s , after 1 min of metal deposition varies significantly between arrays with greater enrichment occurring for smaller trench widths where greater area reduction has occurred. The maximum accelerator coverage for the 1:2 array is ≈ 0.36 with bottom-up filling still actively underway whereas for the 1:1.5 and 1:1 arrays, θ_s is in decline to ≈ 0.28 and ≈ 0.174 , respectively, due to area expansion following inversion of the growth front. It should be recognized that the predicted shape change transitions are a direct reflection of the initial SPS/MPS coverage established by derivatization and thus subject to variation thereof. Further dispersion is possible due to variations in the hydrodynamics and the effective boundary layer width that will influence the rate of features filling.

After 3 min of deposition (Fig. 3c) the trenches are overfilled and the growth front for the 1:1.5 and 1:1 arrays have largely flattened following interaction between the growth fronts emerging from neighboring trenches. In contrast, the convex overburden for the 1:5 and 1:3 trench arrays represent the first cycle of inversion to form a convex growth front. For the filled 1:3, 1:2 and 1:1.5 arrays that have approached planarity the redistribution of Au@SiO_{2-x} particles enriched along the center of the trench reflect the history of area reduction during superconformal filling. Likewise, the Au M _{$\alpha\beta$} EDS maps, Figs. 4c and S17, show the largest signal is now above the trenches, best seen by comparison to the original peak positions in Fig. 4a. Comparison of the Au M _{$\alpha\beta$} EDS maps across the entire trench pattern before and after 3 min of deposition reveal effective conservation of the Au@SiO_{2-x} nanoparticle population with exception of the finest 1:1 trench array where some particle trapping occurred as noted above. Assuming complete conservation of the Au@SiO_{2-x} nanoparticles the enrichment factor across the trench arrays is well captured by comparing the Au M _{$\alpha\beta$} associated with original trench width and location, where the particles originally on the sidewalls have been redistributed and mixed with those on the trench bottom in accordance with area reduction. The expected geometrical enhancement factors (EF_{geo}) for Au@SiO_{2-x} nanoparticle coverage after void-free conversion of the trench array to a planar surface are 1.36, 1.66, 2.00, 2.33, 2.60 for the 1:10, 1:5, 1:3, 1:2 and 1:1.5 features, respectively (Table II). Figure 6a serves as a schematic for the geometrical enhancement factor of the 1:3 and

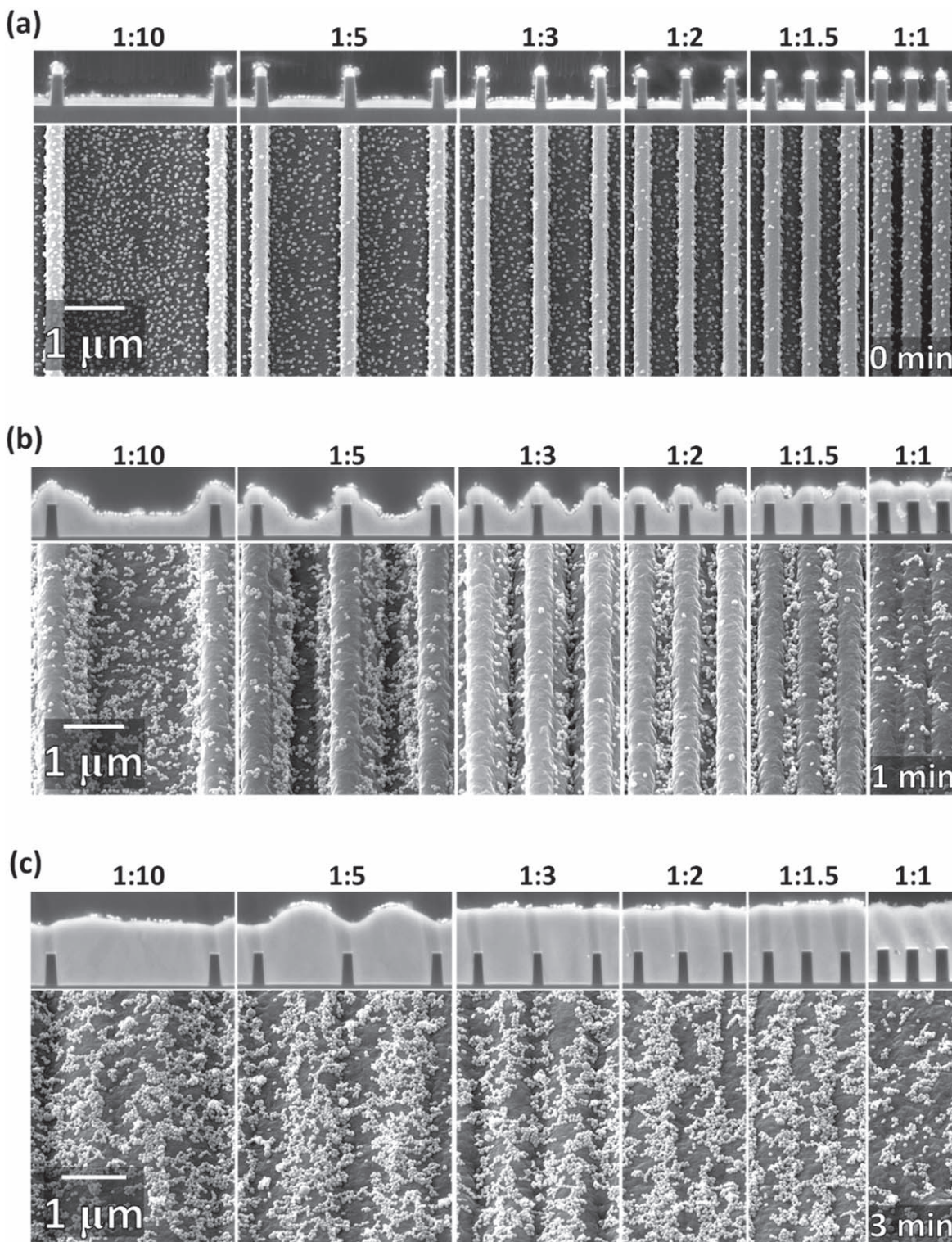


Figure 3. Cross-section and perspective (45° from surface normal) SEM images of trench arrays after (a) 0 min (b) 1 min and (c) 3 min of Cu electrodeposition.

1:1.5 trench arrays. Evaluation of the ratio of the Au $M_{\alpha\beta}$ maps following Cu deposition (Fig. S17), against that for the derivatized surface, yields favorable agreement with the anticipated geometrical enrichment factor as indicated in Fig. 6b. Here the result shown is based on integration of the signal from within the width of the trench to exclude the non-planar trench wall geometry of the derivatized reference specimen.

Before proceeding further, the impact of the Au@SiO_{2-x} nanoparticles on the Cu deposition process itself is assessed. For

higher particle coverages, an obvious concern is screening of the reactant flux and alteration of the associated boundary and double layer conditions at the sub-100 nm scale. The $2.3 \text{ nm} \pm 0.2 \text{ nm}$ thick silica shell is thin enough that weak electronic coupling of the Au nanoparticle with the substrate can support redox processes albeit with somewhat diminished tunneling probability.³⁹ Nucleation of Cu on the silica surface is likewise expected to have a lower probability although contributions to the $\text{Cu}^{2+}/\text{Cu}^+$ electron transfer reaction cannot be ruled out. In the present work each wafer fragment

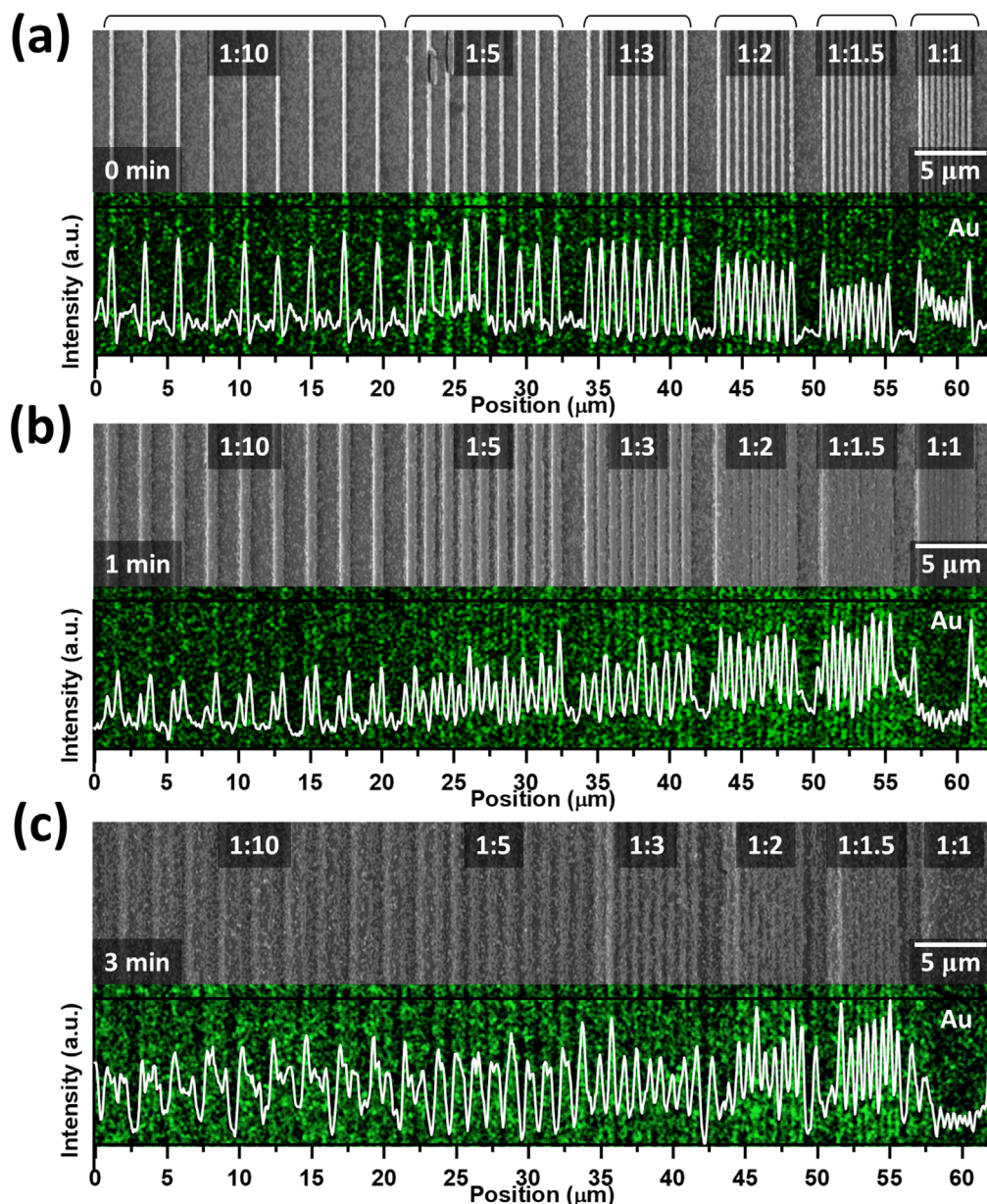


Figure 4. SEM images (top) and maps of Au $M_{\alpha,\beta}$ signal intensity (bottom) with overlaid integrated intensity binned parallel to the trench for (a) 0 min, (b) 1 min, and (c) 3 min of Cu electrodeposition.

contained many repeat patterns of the same trench arrays enabling direct visualization of the impact of Au@SiO_{2-x} nanoparticles on feature filling dynamics by comparison with neighboring Au@SiO_{2-x} nanoparticle-free regions. The Au@SiO_{2-x}-free trench regions shown in Fig. S18 reveal very similar shape evolution during the trench filling experiments indicating that Au@SiO_{2-x} nanoparticles do not significantly alter the bottom-up superconformal growth dynamic, at least for the conditions examined herein. For a fully comprised Damascene plating bath, additional interference or complication associated with the homogenous chemistry between dissolved SPS/MPS accelerator and Cu⁺ at small overpotentials might arise that, by design, are avoided and not evident in the present experiment.

Au@SiO_{2-x} enhanced raman spectroscopy from superfilling cu trenches.—The effectiveness of Au@SiO_{2-x} nanoparticles as Raman spectroscopy reporters of local surface chemistry during superconformal Cu electrodeposition was examined. As a first step towards future *in operando* measurements, the electroplated trench

arrays were examined ex situ under an Ar atmosphere. As with the study of planar specimens, following Cu deposition at $-0.625 V_{SSE}$ the trench patterned specimens were rinsed with H₂ purged 4 μmol l⁻¹ HCl to remove the residual electrolyte while hindering Cl⁻ desorption from the surface. Mapping experiments were performed by incrementally rastering the laser over a series of trenches in a defined grid pattern (Fig. S19) while collecting Raman spectra at each node. The area mapped was 74 μm by ≥18 μm with 2 μm increments between each point, this being larger than the estimated ≈ 1 μm probe size of the laser. Therefore, each map was composed of at least 380 spectra, 38 points in a row and at least 10 rows (Fig. S19). A 3 s acquisition time with 50% laser power (theoretical power of ≈ 2.5 mW μm⁻²) was used to collect each spectrum. The mapped regions overlap the Au@SiO_{2-x} nanoparticle covered trench arrays detailed in the previous section. Plentiful fiduciary marks associated with the patterned trench arrays, like that shown in Fig. S14, enable good spatial alignment and correlation between the different measurements. Spectra were primarily collected from 150 cm⁻¹ to 1100 cm⁻¹ and 2750 cm⁻¹ to 3080 cm⁻¹. Peaks of interest were

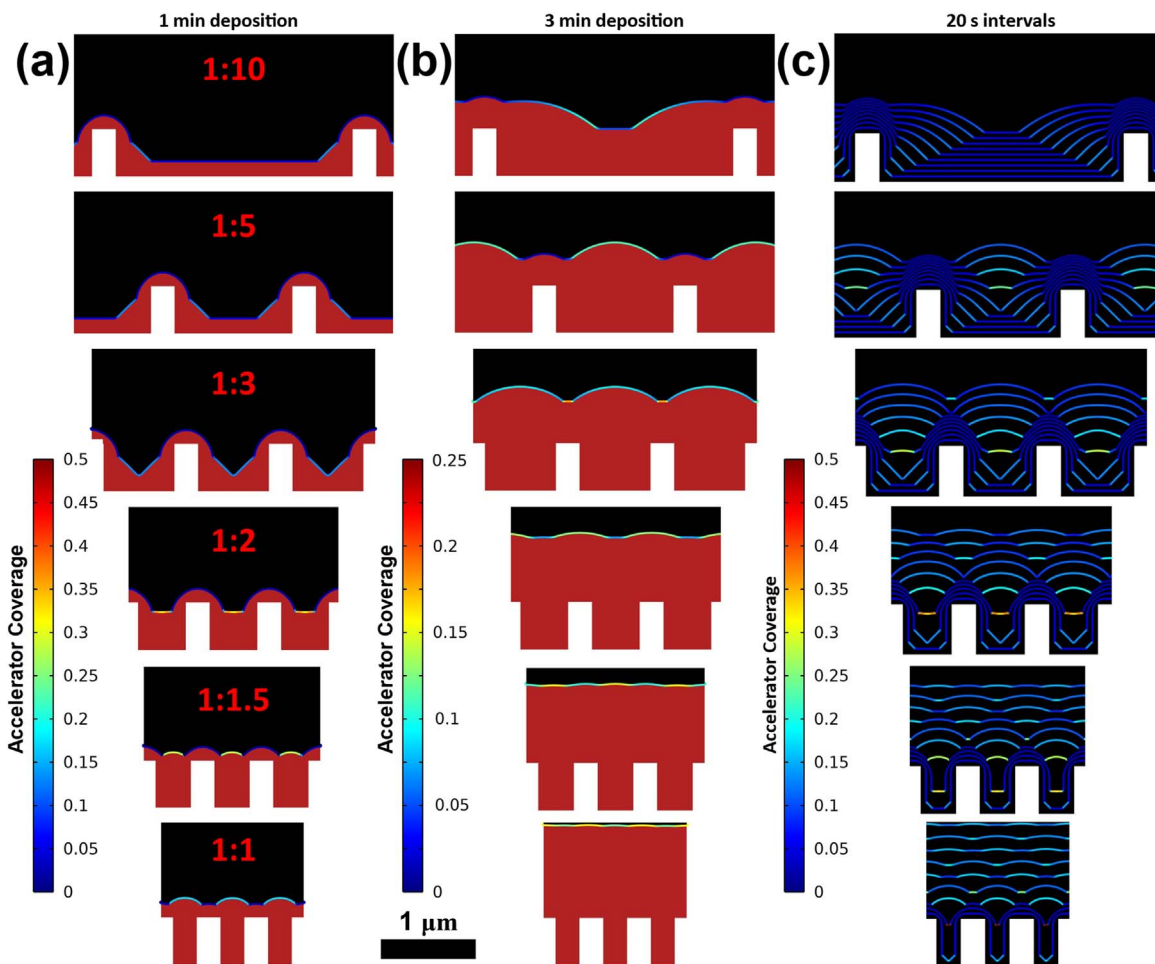


Figure 5. CEAC simulations predicting the amount of Cu deposited and the surface concentration of SPS after (a) 1 min, (b) 3 min or (c) 20 sec intervals of Cu electrodeposition with an initial accelerator coverage (θ_0) of 0.05.

selected, and spectral windows truncated to enable low order polynomial background fits (e.g. linear) after which each peak was integrated with a range similar to that reported (Fig. 1f). Heat maps aligned and superimposed on the trench arrays allow comparison of the integrated peak area for each mesh position (Fig. S19) as shown in Figs. 7a–7c.

Three trench patterned samples were examined in detail, one with no exposure to the SPS accelerator (negative control) but subject to Cu electrodeposition at -0.625 V_{SSE} for 1 min in the presence of PEG and Cl[−] (Fig. 7a), and two specimens derivatized with 30 s of exposure to $50 \mu\text{mol l}^{-1}$ SPS solution followed by electroplating for 1 min (Figs. 7b) or 3 min (Fig. 7c) in the presence of PEG and Cl[−]. The maps in the top row represent the convolution of the local Cl[−] coverage with the variation in enhanced Raman generation provided by the different arrangements of the Au@SiO_{2−x} nanoparticles. For non-planar surface segments the degree of enhancement increases as neighboring nanoparticles interact more strongly as the particle-particle spacing decreases.⁴⁰ Further plasmonic enhancements associated with the nanoscale concave surfaces that develop during trench filling are also possible.^{40,41} For the present system, the adsorbed Cl[−] coverage is propitiously close to saturation such that the ν_{CuCl} band can be used as an internal reference for assaying the local Au@SiO_{2−x} nanoparticle coverage and/or fluctuations in enhancement associated with the Au@SiO_{2−x} particle-particle contact density.³⁷

The Raman map, Fig. 7a, collected after Cu electrodeposition in the presence of PEG-Cl reveals a distribution of ν_{CuCl} hot spots across the trench arrays. For these conditions Cu deposition leads to

conformal growth and the ν_{CuCl} intensity variations are attributed to clustering of Au@SiO_{2−x} nanoparticle coverage due to wetting variability during dropcasting of the Au@SiO_{2−x} nanoparticles on the Cu seed layers; the initial variability in Au@SiO_{2−x} nanoparticle coverage being at least partly related to the extended storage of the Cu seeded wafer and its fragments in the laboratory ambient. This contrasts to the more uniform distribution of Au@SiO_{2−x} nanoparticles dropcast on hydrophilic SPS derivatized surfaces shown in Fig. 3a. Following 1 min of Cu deposition on the SPS-derivatized specimen, ν_{CuCl} hot spots are evident on the 1:1.5 trench arrays (Fig. 7b). SEM images on a similar, although not identical, sample region, Fig. 3b, indicate that the strong Cl[−] signal is associated with the extended array of Au@SiO_{2−x} nanoparticles aligned along the still recessed, but emerging concave growth front of the 1:1.5 trench array with an approximate radius of 100 nm. For 3 min of Cu deposition the location of the strongest ν_{CuCl} signal shifts to the wider 1:5, 1:3 and 1:2 trench arrays and SEM reveals extended alignment of Au@SiO_{2−x} nanoparticle arrays along the centerline of the superfilled trenches.

Building upon the Raman enhancement associated with the densification of Au@SiO_{2−x} nanoparticles by area reduction enables the similar enrichment of the SPS-derived accelerator to be revealed by mapping the ratio of ν_{RSO} at 1033 cm^{-1} to the 300 cm^{-1} ν_{CuCl} band. For Cu deposition on the SPS-free specimen in the presence of PEG-Cl, Fig. 7a, negligible signal at 1033 cm^{-1} was observed. In contrast, for SPS-derivatized specimens the accelerator is clearly present on the electrodeposited Cu surface. Following 1 min of deposition the highest ν_{RSO} intensity is associated with the 1:1.5

Table II. Enhancement factors for trench arrays after 1 min of Cu electrodeposition.

1 min		Theory		SEM-EDS Au $M_{\alpha,\beta}$ EF	Raman	
Trench Ratio	Geometric EF	CEAC Model Entire Profile	CEAC Model Au@SiO _{2-x} Dense Regions		EF _{RSO/Cl}	XPS
1:10	1.36	1.15	1.28	0.80 ± 0.15	1.51 ± 0.1	—
1:5	1.67	1.27	1.70	0.92 ± 0.18	1.91 ± 0.2	—
1:3	2	1.41	2.57	2.79 ± 0.41	1.90 ± 0.1	—
1:2	2.33	2.15	6.29	3.25 ± 0.62	2.43 ± 0.11	—
1:1.5	2.6	2.40	5.40	3.27 ± 1.57	2.97 ± 0.16	—
1:1	3	2.58	2.58 ^{b)}	0.95 ± 0.15	2.82 ± 0.2	—
All	1.84/1.62 ^{a)}	1.54	2	1.48 ± 0.33	2.03 ± 0.14	1.43 ± 0.39

a) Ignoring contributions from 1:1 trenches since particle entrapment is observed. b) No dense regions of Au@SiO_{2-x} nanoparticles observed.

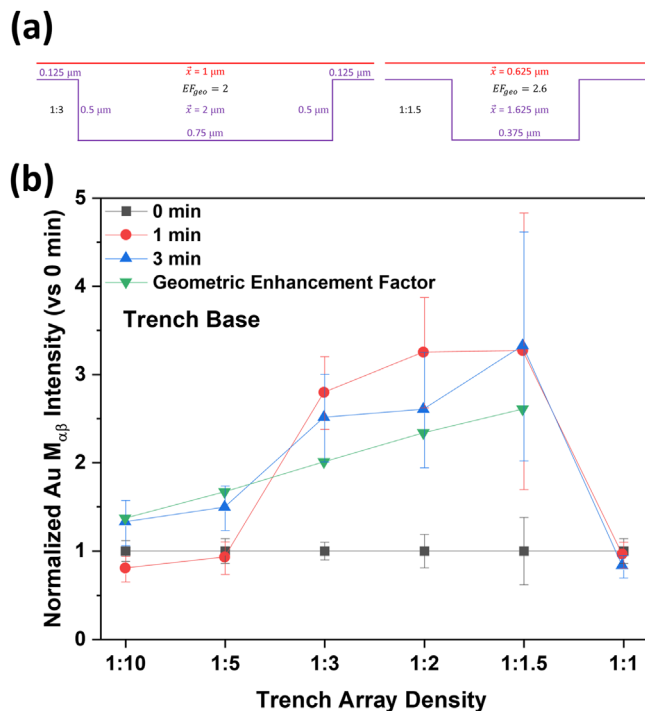


Figure 6. (a) Schematic of geometric enhancement factor for ideal conservation of the surfactant and/or Au@SiO_{2-x} coverage during the filling of the 1:3 and 1:1.5 trenches as the initial trench profile, (purple line) is converted to an idealized planar film (red line) (b) Comparison of geometric enhancement factor vs the Au M_{α,β} intensity from Au@SiO_{2-x} EDS mapping measurements (Fig. S17b) following 1 min and 3 min of deposition. The error bars represent the standard deviation of the measurement.

trenches congruent with the enrichment and clustering of the Au@SiO_{2-x} nanoparticles on the bottom-up growth front consistent with the SPS/MPS enrichment predicted by the CEAC shape change model. A similar trend, albeit with lower signal to noise, is observed for the *trans* ν(C-S)_{RS} peak at ≈680 cm⁻¹ (Fig. S20) when normalized to ν_{CuCl}. It remains to be determined if further plasmonic coupling with the concave growth front provides additional enhancement of the Raman signal analogous to that reported for nanoparticles in cavities of similar dimensions.^{37,40,41} Following 3 min of Cu deposition the location of the maximum ν_{RSO}/ν_{CuCl} signal (Fig. 7c) shifts from the 1:1.5 to the 1:3 trench arrays where SEM images reveal a high density of Au@SiO_{2-x} nanoparticle clusters aligned along the centerline of the overburden above the filled trenches (Fig. 3c). Based on the normalization procedure and comparatively flat morphology of the filled trench arrays with the rows of aligned Au@SiO_{2-x} nanoparticles, the enhanced ν_{RSO} signal reflects the enrichment of SPS/MPS derived accelerator θ_S that accompanies reduction of the growth front area.

Two positive controls for SPS-derivatized trench arrays were examined: one exposed to 50 μmol l⁻¹ SPS — 0.1 mol l⁻¹ H₂SO₄ for 30 s, while the other involved exposure to a more concentrated accelerator solution of 1 mmol l⁻¹ SPS — 100 μmol l⁻¹ HCl — 0.1 mol l⁻¹ H₂SO₄ for 30 s. For the standard derivatization treatment the ν_{CuCl} map (Figs. S21a, S21c) shows the Cl⁻ signal decreases gradually from the 1:10 to 1:1 trenches presumably due to a falloff in the density of Au@SiO_{2-x} particles. Importantly, when the ν_{RSO} map is normalized against ν_{CuCl} the resulting ν_{RSO}/ν_{CuCl} map is comparatively uniform with random variation in the ratio between 0.1 and 0.3. Averaging over every point in the map for the derivatized patterned sample yields a ν_{RSO}/ν_{CuCl} ratio of 0.21 ± 0.05 comparing favorably to the derivatized planar surface in Fig. 1f. Derivatization in more concentrated SPS solution results in higher average ratio ν_{RSO}/ν_{CuCl} of 0.42 ± 0.12 and much larger dispersion between 0.3 and 0.6 across the workpiece.

The ν_{RSO}/ν_{CuCl} maps were analyzed further by binning the data for the individual trench arrays as indicated in Figs. S19 and 7 and the average ν_{RSO}/ν_{CuCl} was evaluated for all grid points within trenches (Fig. 8a). The 0.022 offset from zero for the SPS free control (Figs. 7a and 8a, yellow squares) agrees with the systematic error related to background noise found in the planar specimens (0.023, Fig. 1f) and is subtracted from ratios for the other specimens discussed in the following text. On the planar electrode the ν_{RSO}/ν_{CuCl} after 1 min and 3 min of deposition was 0.073 (0.096–0.023) and 0.069 (0.092–0.023), respectively, which is less than the average ratio across the entire SPS-derivatized trench array specimens of 0.148 (0.17–0.022) and 0.118 (0.14–0.022), respectively. The enrichment reflects the collection of accelerator from the trench sidewalls during the upward motion of the growth front during Cu deposition. A similar enrichment relationship is observed between 1 min and 3 min for *trans* ν(C-S)_{RS}/ν_{CuCl} (Fig. S22), albeit again with lower signal to noise. Assuming complete segregation of the accelerator to the growth surface during deposition should yield an effective enrichment factor, EF_{geo} (Eq. 1), of 1.62 for filling over the whole 1:10 to 1:1.5 trench array pattern (Table II); the void prone 1:1 features not being considered. The ratio between patterned and planar samples for each increment of deposition yields the measured enrichment factor, EF_{RSO/Cl} (Eq. 2), and gives 2.03 after 1 min and 1.71 after 3 min of Cu deposition. The later value is close to the simple estimate based on the final filled trench geometry that does not consider the dependence of the Raman enhancement on the spacing of the nanoparticle reporters (Table II and SV).

$$EF_{geo} = |x_{length}| + |y_{length}|/x_{length} \quad [1]$$

$$EF_{RSO/Cl} = \left(\frac{\nu_{RSO}}{\nu_{CuCl}} \right)_{pattern} / \left(\frac{\nu_{RSO}}{\nu_{CuCl}} \right)_{planar} \quad [2]$$

XPS was also used to examine similar trench patterned specimens (Figs. 8b–8d) although a much larger elliptical area 700 μm × 300 μm was assayed. The major axis is aligned with the 2510 μm-long trenches, while the minor axis incorporates four complete sets of the trench arrays with the trench side wall systematically decreasing in steps, 250 nm, 220 nm, 200 nm, and 180 nm. The ratio of θ_S/θ_{Cl} for the trench filling experiment is compared with the results for the planar electrodes in Fig. 8b. The average θ_S/θ_{Cl} following 1 min, 2 min, and 3 min of Cu electrodeposition in the trench patterned arrays are higher than for the planar surface. The error bars represent the standard deviation between measurements on three independent trench filling experiments. Taking the ratio between the trench patterned and planar surface yields an enhancement factor of 1.43 ± 0.39, 1.67 ± 0.46 and 1.10 ± 0.46 following 1 min, 2 min, and 3 min of Cu deposition (Tables II and Table SV).

Compared to conventional XPS, Raman microscopy enables examination of the individual arrays as summarized in Fig. 8a. After 1 min of Cu deposition a substantial increase in ν_{RSO}/ν_{CuCl} is evident for the higher aspect ratio 1:2, 1:1.5 and 1:1 trenches. For the 1:1.5 trenches, the ν_{RSO}/ν_{CuCl} is 0.217 (0.239–0.022), nearly 3 times that of the planar surface congruent with an EF_{geo} of 2.6 (Table II). The CEAC simulation that also considers additive incorporation predicts a slightly lower enhancement factor of 2.4 for the 1:1.5 array (Table II). In contrast, the overall enrichment is far less in the lower aspect ratio features as during the first minute of deposition only the lower corners have experienced significant area reduction. After 3 min of deposition the prior enrichment of the accelerator over the finer features is attenuated as the emerging growth front dilates followed by growth front curvature oscillations as neighboring trenches begin to interact with one another as evident in the simulation shown in Fig. 5c. On the other hand, filling of the lowest aspect ratio features is just complete with Au@SiO_{2-x} nanoparticles concentrated along the centerline of the former trenches on what is now a more planar surface profile. Taking the ratio of the measured ν_{RSO}/ν_{CuCl} to that for the planar surface detailed in Fig. 1 yields

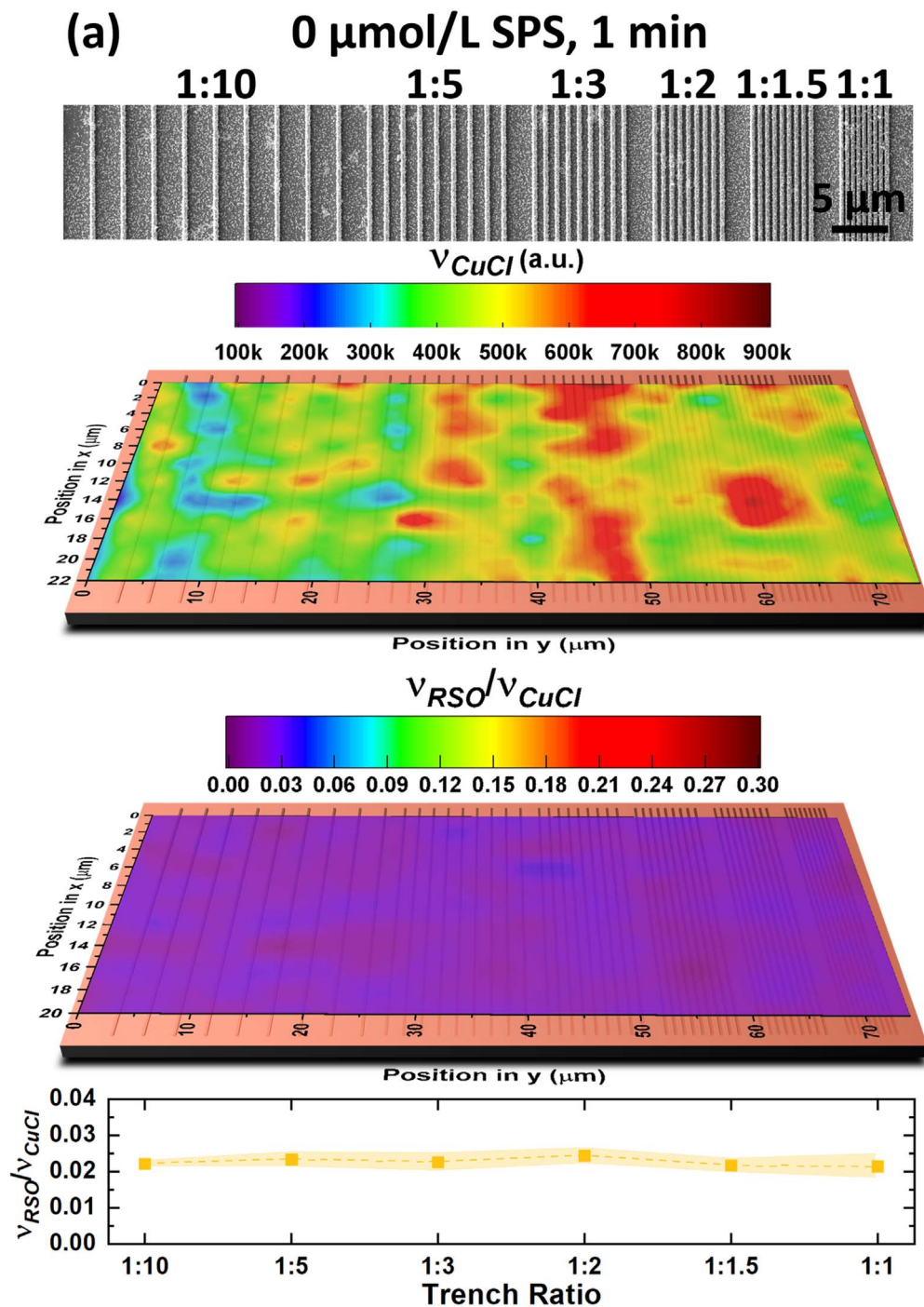


Figure 7. Raman mapping experiments of (a) a fresh Cu seeded surface (no SPS) after 1 min of Cu deposition and (b,c) derivatized in 50 $\mu\text{mol l}^{-1}$ SPS for 30 s followed by (b) 1 min and (c) 3 min of Cu electrodeposition. Each panel consists of a top-down SEM image of the 6 trench arrays, Raman maps of the ν_{CuCl} peak area, peak area ratio $\nu_{\text{RSO}}/\nu_{\text{CuCl}}$ and average $\nu_{\text{RSO}}/\nu_{\text{CuCl}}$ binned by trench array (Fig. S19). The shaded regions in the binned plots represent the standard deviation between grid columns.

enhancement factors for the filled trenches of 1.58 (0.109/0.069) for 1:10, 1.76 (0.121/0.069) for 1:5 and 1.84 (0.127/0.069) for 1:3 that compare to the ideal values of 1.36, 1.67 and 2.0, respectively, for complete accelerator conservation (Table SV).

The ideal surfactant approximation (EF_{geo}) has two limitations: it does not consider decomposition and incorporation of the accelerator species into the growing deposits and does not account for the uneven distribution of Au@SiO_{2-x} nanoparticles causing variations in Raman enhancement. The CEAC simulations enable closer examination of the impact of these effects. If the SPS coverage along each trench array is integrated and averaged over the surface

in the x-direction (Figs. S23–S24) (e.g. ignoring the variation of the growth front position in the y-dimension, similar to the Raman analysis) the resulting average θ_{S} coverage (Fig. 9a) increases monotonically as trench width decreases with the coverage being slightly higher after 3 min of deposition (Fig. 5). However, this trend does not fully correlate with that observed *via* SHINERS measurements (Fig. 8a), specifically the SHINERS measurements report lower $\nu_{\text{RSO}}/\nu_{\text{CuCl}}$ for all trench ratios after 3 min of electrodeposition in comparison to 1 min. However, the Raman signal is likely correlated with regions of higher Au@SiO_{2-x} nanoparticle coverage. These regions can be identified in top-down and

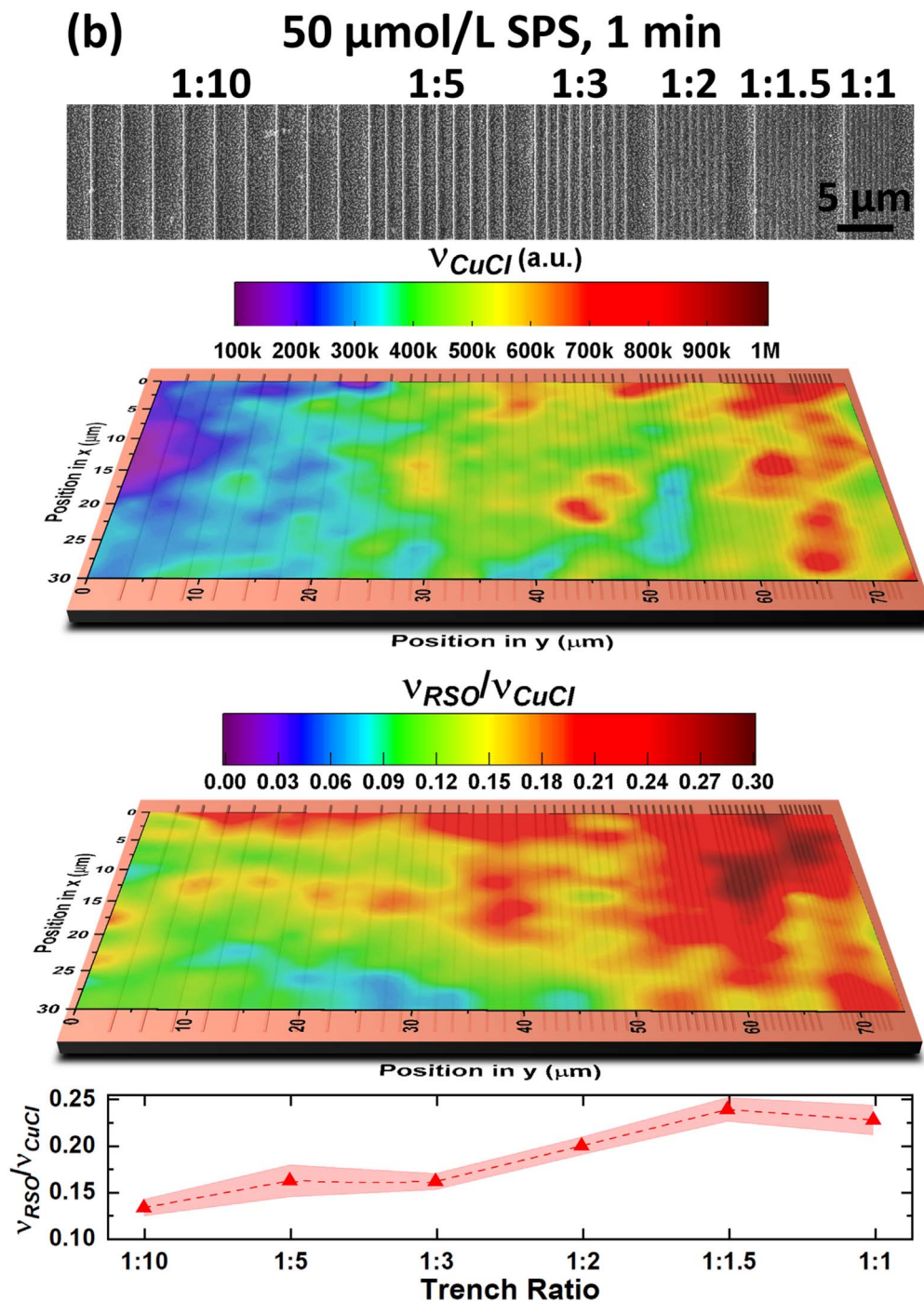


Figure 7. (Continued.)

cross-sectional SEM images, (Figs. 3 and S18). By averaging the SPS coverage from the CEAC model over this subset of regions (shaded in Figs. S23–S24) more favorable agreement is obtained between the Raman measurements and the CEAC model (compare Fig. 8a with Fig. 9b vs Fig. 9a). This correlation is congruent with the regions most enriched with accelerator, θ_S , accounting for the strongest bottom-up filling. As with the SPS derived accelerator, the enrichment of Au@SiO_{2-x} nanoparticles coverage is greatest in regions where significant area change has occurred (Figs. 3, S18, S23 and S24). Following 1 min of Cu deposition, the inflection and increase in $\nu_{\text{RSO}}/\nu_{\text{CuCl}}$ for the 1:3, 1:2, 1:1.5 trench arrays shown in Fig. 9b corresponds to the onset of sidewall collisions and the

transition to bottom-up filling that correlates to higher local θ_S and the 2-D coalescence of the Au@SiO_{2-x} reporters responsible for the enhanced Raman yield. What, if any, additional role the local concave curvature may exert in the enhancement remains to be determined. In contrast, following 3 min of deposition the trenches are all filled and both the locally enhanced θ_S and nanoparticle density associated with bottom-up filling are now in decline with the variation in θ_S for each binned trench width being much smaller consistent with the measured $\nu_{\text{RSO}}/\nu_{\text{CuCl}}$.

Tracking competitive accelerator and suppressor adsorption via methylene modes.—Analysis of the methylene spectra (Table I $\geq$

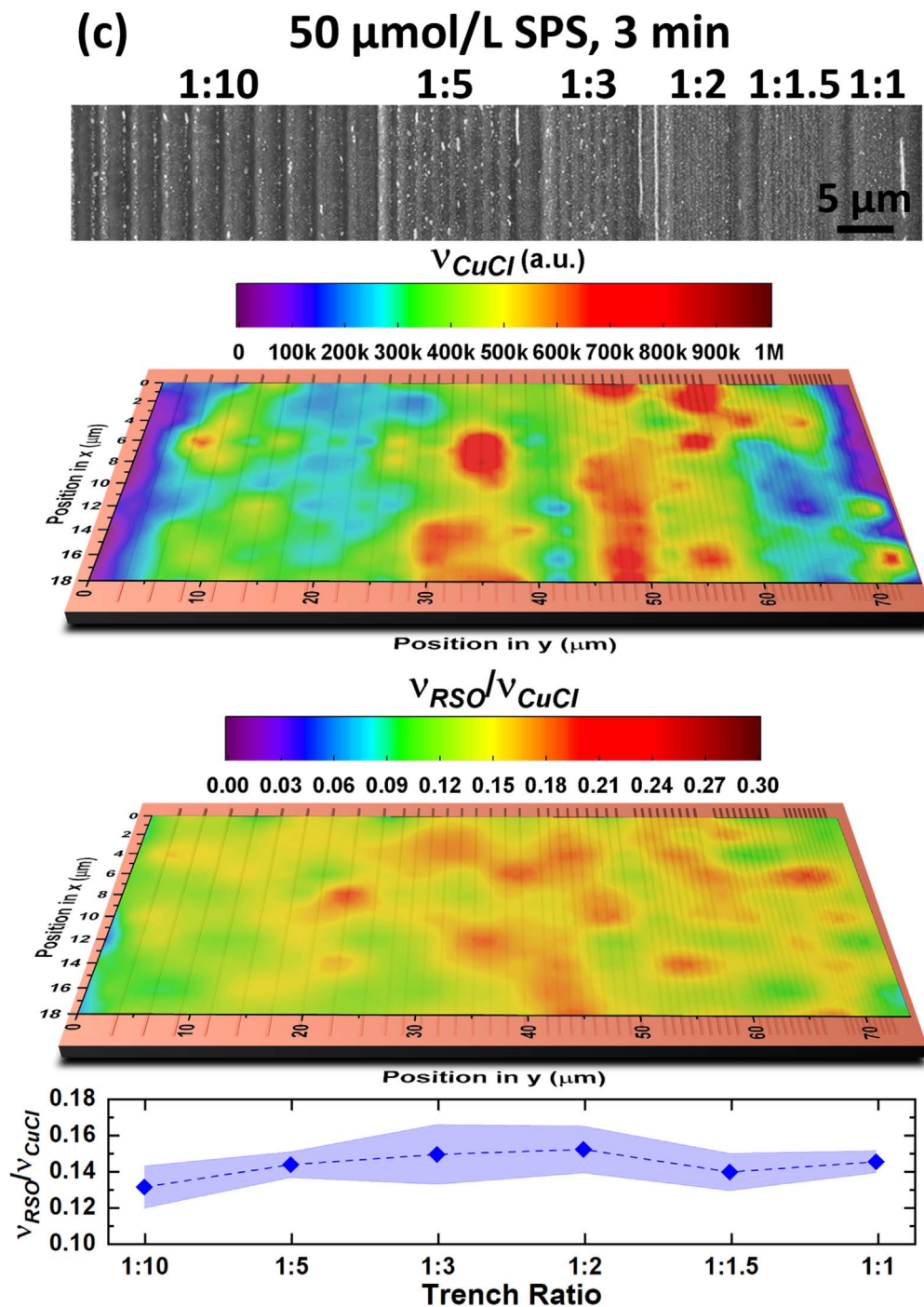


Figure 7. (Continued.)

2850 cm^{-1}) is more complex as it includes contributions from both the propane chain ($n = 3$) of the SPS/MPS accelerator species and the polyethylene glycol suppressor ($n = 77$). Nevertheless, the spectra for the respective dissolved molecules are distinct, (Fig. S7). Following Cu deposition on an SPS-free surface or SPS-derivatized surface the methylene band is comprised of several components, Fig. S8, Fig. 10 and Table I. Peak assignments for the polyether suppressor were drawn from the literature⁵ with a focus on the position and intensity of the two most prominent components, $\approx 2920\text{ cm}^{-1}$ and $\approx 2940\text{ cm}^{-1}$ of the multicomponent band. The 2920 cm^{-1} peak was dominant in the SPS-derivatized samples and its presence after 1 min and 3 min of deposition correlates to

solvated methylene species congruent with the dilute coverage of SPS/MPS species. The methylene spectra for the electrodeposit grown solely in the presence of PEG-Cl⁻ shows its strongest component peak at 2940 cm^{-1} congruent with the asymmetric methylene stretch previously reported in a Raman study of PEG adsorption on a roughened Cu electrode with 100 ppm PEG solution.⁵ This result is also congruent with surface enhanced infrared spectroscopy (SEIRAS) measurements that suggest polyethylene glycol orients the carbon chain backbone towards the relatively hydrophobic Cl-covered Cu electrode while the ether oxygens are oriented towards the electrolyte to enable maximum hydrogen-bonding interactions that sum to minimize the surface free

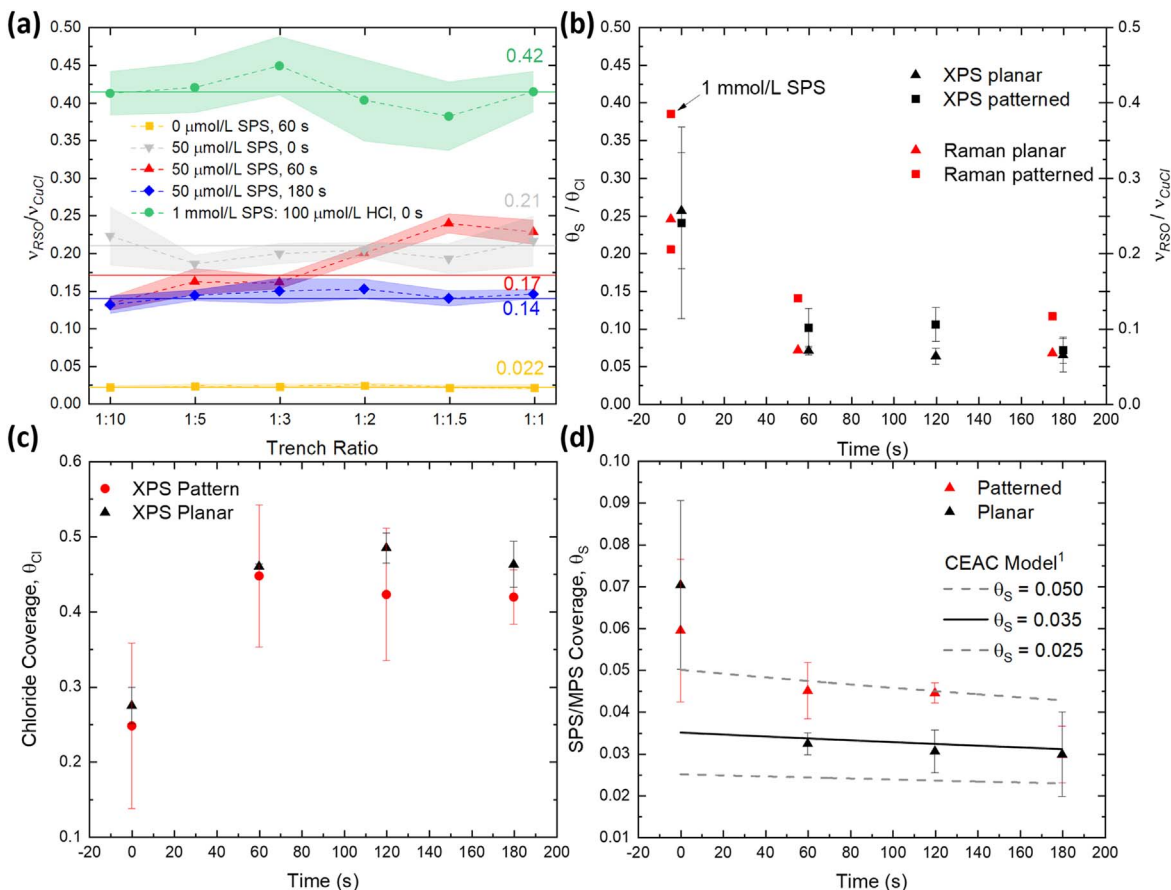


Figure 8. (a) Binned $\nu_{\text{RSO}}/\nu_{\text{CuCl}}$ ratio from Raman mapping experiments over patterned trench arrays. (b) $\theta_{\text{S}}/\theta_{\text{Cl}}$ ratio from XPS, (c) chloride coverage from XPS and (d) SPS/MPS coverage from XPS compared to CEAC predictions for a planar surface.¹ The shaded regions in (a) represent the standard deviation between grid columns (Fig. S19), for a given trench ratio, while the solid lines represent the average ratio from all grid points within trenches.

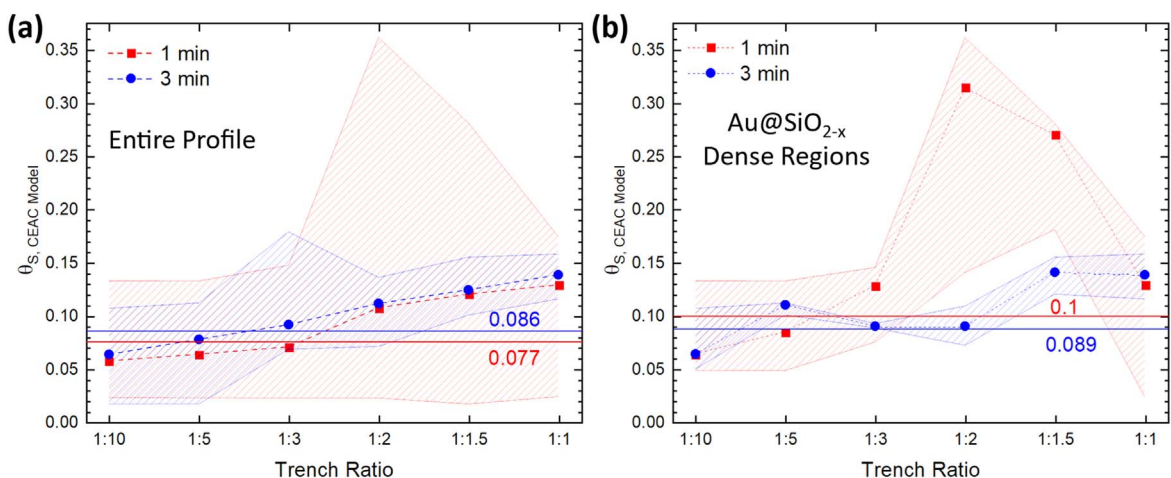


Figure 9. Average SPS coverage over (a) the entire growth front profile and (b) at Au@SiO_{2-x} dense regions from the CEAC model. Au@SiO_{2-x} dense regions were determined from cross-section images, e.g. Fig. 3. The transparent dashed regions depict the minimum and maximum θ_{S} across the growth front profile, see Figs. S23–S24, respectively. The solid red and blue lines represent the average SPS coverage over the entire patterned array for 1 min and 3 min, respectively.

energy.⁶ The intensity ratio of the 2920 cm^{-1} to the 2940 cm^{-1} peak for each specimen (Fig. S25) reflect the relative coverage of SPS as the SPS free $\ll$ 1 min $\approx$ 3 min $\ll$ 50 $\mu\text{mol l}^{-1}$ SPS derivatization $\approx$ 1 mmol l^{-1} SPS derivatization as determined by $\nu_{\text{RSO}}/\nu_{\text{CuCl}}$ Raman and XPS measurements.

Raman maps were constructed for the $\nu_{\text{CH}}/\nu_{\text{CuCl}}$ ratio based on integration of the entire methylene envelope (ν_{CH}) and binned for each trench array. In the absence of SPS, $\nu_{\text{CH}}/\nu_{\text{CuCl}}$ was uniform and

slightly greater than ≈ 0.7 for all six trench arrays after 1 min of Cu deposition in the presence of the PEG-Cl suppressor combination. In contrast, $\nu_{\text{CH}}/\nu_{\text{CuCl}}$ decreased significantly for Cu deposition on the SPS-derivatized electrodes (Fig. 11a) as SPS adsorption leads to a more hydrophilic surface that inhibits adsorption of the polyether suppressor. Smaller and less significant differences with feature size are evident between 1 min and 3 min of Cu deposition. A similar trend is evident in XPS measurements for the planar specimens

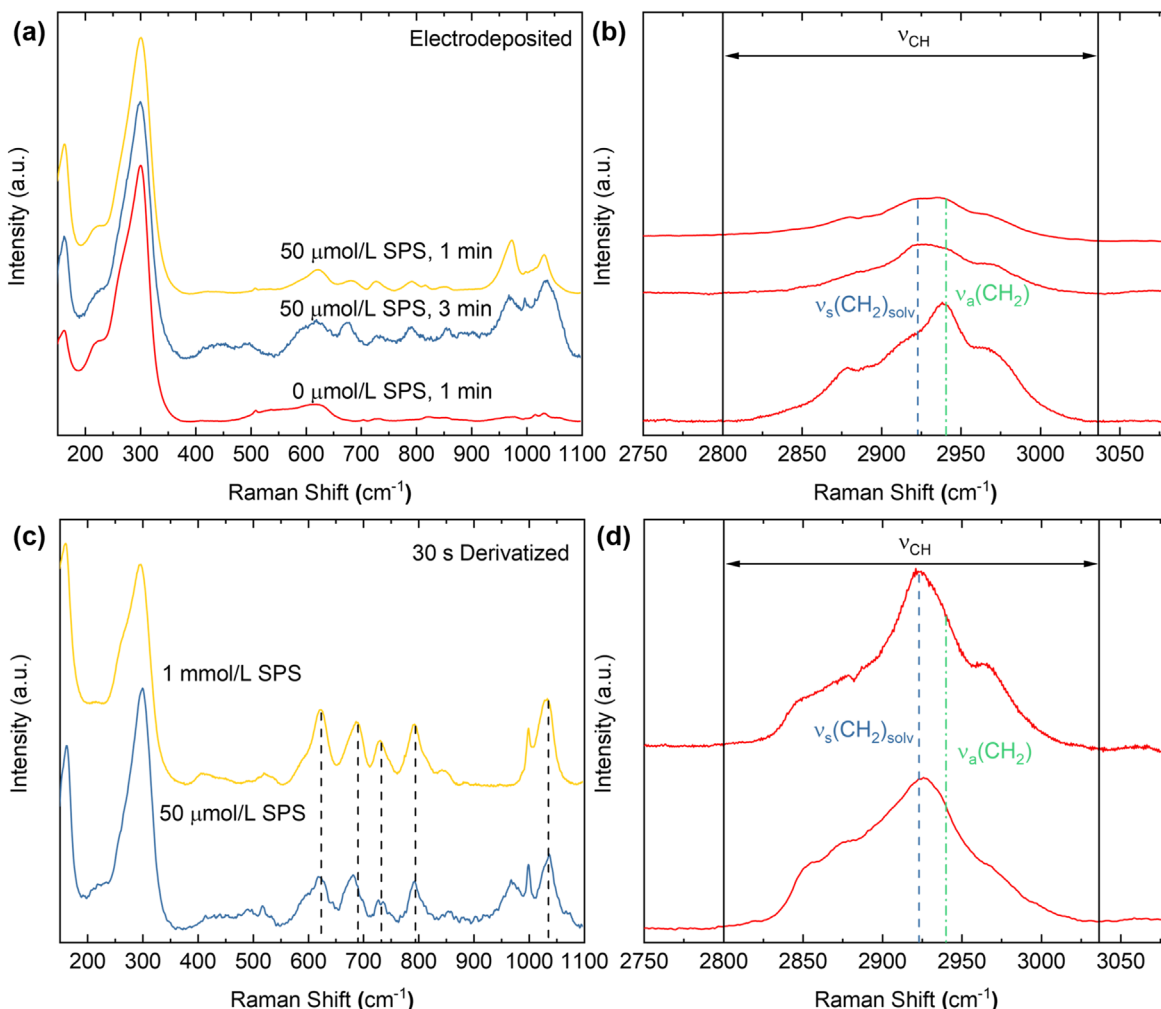


Figure 10. Average Raman spectra from (a–b) electrodeposited samples and (c–d) derivatized samples showing global vibrational behavior from (a,c) 150 cm^{-1} to 1100 cm^{-1} and (b,d) 2750 cm^{-1} to 3100 cm^{-1} . Spectra intensity were scaled to that of ν_{CuCl} .

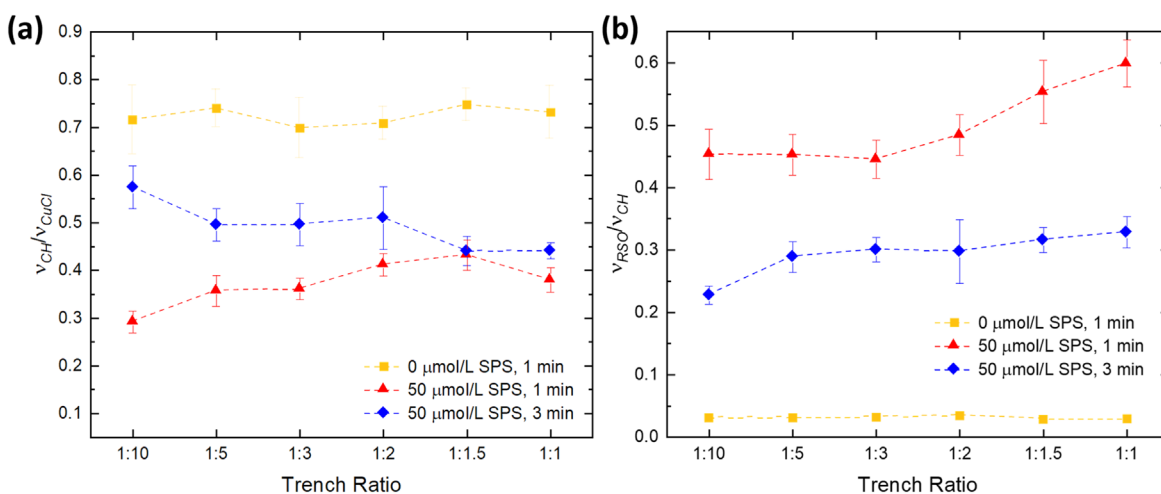


Figure 11. Average ratio for (a) ν_{CH} vs ν_{CuCl} and (b) ν_{RSO} vs ν_{CH} of each respective trench array for samples with different derivatizations and electrodeposition times. The error bars in represent the standard deviation between grid columns (Fig. S19), for a given trench ratio.

where the polyether is evident with a distinct contribution at 286 eV in the $\text{C}(1\text{ s})$ spectra (Figs. S10d, S11d, S12d). Following Cu deposition on an SPS-derivatized electrode the polyether component is substantially reduced below that observed after electroplating on a SPS-free surface. Tracking the ratio of the sulfonate stretch to the

methylene band, $\nu_{\text{RSO}}/\nu_{\text{CH}}$ reveals a general increase with a decrease in trench width (Fig. 11b). Following 1 min of deposition the ratio is flat for the widest feature that has experienced limited area reduction while a monotonic increase for the finer trench arrays is consistent with the increasing accelerator coverage from area reduction and the

corresponding decrease in suppressor coverage. After 3 min of deposition all the trenches are filled with a monotonic rise in ν_{RSO}/ν_{CH} evident across the flattened trench array surface.

The assembly and rearrangement of Raman reporters by area change is a particularly useful tool for selectively probing the local surface chemistry associated with superconformal deposition as well as the production of bright specular surface coatings. Cross referencing Raman experiments on planar surfaces with XPS enables the surface coverage to be independently quantified. The global impact of area change on adsorbate coverage of an engineered substrate can be quantified by conventional XPS measurements while Raman mapping reveals variation at the micrometer, and even sub-micrometer, range. As Raman enhancement is associated with coupling between adjacent nanoparticles and the surface, tuning the initial Au@SiO_{2-x} coverage relative to anticipated area reduction should enable further optimization of spatial sensitivity by creating Raman hot spots in regions of high concave curvature where superconformal feature filling dynamics are most intense. Further still, the Raman approach enables *in operando* measurements of active deposition processes that are beyond the reach of vacuum methods and the focus of on-going work.

Broadening to other applications varying the nanoparticle surface chemistry should enable the study and optimization of nanoparticle binding interactions, both covalent and non-covalent, relevant to competitive and co-adsorption phenomena and their combined impact on morphological evolution during electrodeposition. The above variations can be used to modulate the propensity of the nanoparticles to float or alternatively, be incorporated into the growing deposit with the latter providing a new avenue for the study of electrodeposition of nanoparticle-metal/oxide/polymer matrix composites.

Conclusions

The application of SHINERS to interrogate the surface chemistry during electrodeposition provides a new opportunity to quantify the accumulation, distribution and functionality of additives that control and determine the evolution of surface morphology. Taking the example of the Cu Damascene electrodeposition process used in the fabrication of microelectronic circuitry, the ability of Au@SiO_{2-x} nanoparticles to float on growing surfaces and report on the local surface chemistry has been demonstrated. Following Cu deposition on SPS-derivatized planar electrodes, good agreement is observed for the accelerator coverage measured by SHINERS, ν_{RSO}/ν_{CuCl} , and the θ_S/θ_{Cl} fractional adsorbate coverage ratio derived from the S 2p low binding energy state and Cl 2p XPS spectra. During Cu deposition chloride is the dominant adsorbate with a coverage near 0.5 relative to the underlying metal lattice while the accelerator coverage is close to ≈ 0.035 for the conditions examined. These values are congruent with those reported for in situ competitive SPS-Cl adsorption studies at similar potentials, but in the absence of metal deposition.

Similar studies of trench patterned specimens demonstrate that the floating nanoparticle reporters respond to area change. Given an initially uniform sub-monolayer distribution of nanoparticles, subsequent area change on recessed concave surfaces such as trench arrays results in the local enrichment of the Au@SiO_{2-x} nanoparticles and development of Raman hot spots. Raman mapping reveals an increase in ν_{RSO}/ν_{Cl} with trench filling whereby, like the nanoparticle reporters, the SPS-derived accelerator on the sidewalls is collected and redistributed upon the advancing bottom-up concave growth front in good agreement with prediction based on the CEAC model. The ν_{RSO}/ν_{CuCl} ratio increases with decreasing feature size from 1:10 to 1:1.5 arrays due to the area driven enrichment of the SPS accelerator. The integrated global enrichment of SPS across the trench arrays captured by SHINERS is in good agreement with that measured by XPS. Accelerator enrichment and the corresponding increase in hydrophilic character leads to a decrease in the polyether coverage as evident by the increasing ν_{RSO}/ν_{CH} ratio and decreasing

286 eV polyether component in the C 1s spectra. The combination of SHINERS and XPS provides a powerful means for investigating the molecular details of superfilling and, more generally, surfactant-mediated growth. Having established that nanoparticles can float on certain types of advancing surfaces, exploration of different chemistries where the opposite circumstance of nanoparticle entrapment in the deposit occurs, promises to open a new avenue in the study of the formation of metal matrix-nanoparticle composites and provide new insights into the nature of nanoparticle-electrode surface chemistry interactions.

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