Bottom-Up Gold Filling in New Geometries and Yet Higher Aspect Ratio Gratings for Hard X-Ray Interferometry

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### ABSTRACT

An extreme bottom-up filling variant of superconformal Au electrodeposition yielding void-free filling of recessed features is demonstrated with diffraction gratings composed of a twodimensional patterned "chessboard" array of square vias of aspect ratio (depth/width)  $\approx 23$  as well as one-dimensional arrays of trenches having aspect ratios exceeding 50 and 65. Deposition on planar and patterned substrates is examined in several near-neutral x mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> + 0.64 mol·L<sup>-1</sup> Na<sub>2</sub>SO<sub>3</sub> electrolytes (x = [0.08, 0.16, 0.32]) containing  $\approx 50 \ \mu mol·L^{-1}$  Bi<sup>3+</sup> additive. The electrolytes are similar to those used in earlier work, although the upper bound on Au(SO<sub>3</sub>)<sub>2</sub> concentration is twofold greater than previously described. Filling results are complemented by associated current and deposition charge transients whose features, particularly with well controlled pH, exhibit repeatable behaviors and timescales for incubation of passive deposition followed by bottom-up, void-free filling. While incompletely filled features can exhibit substantial via-to-via variation in fill height, self-passivation that follows complete bottom-up filling results in highly uniform filling profiles across the substrates. Visibility measurements capture the quality and uniformity of the as-formed wafer scale gratings. X-ray phase contrast imaging demonstrates their potential for imaging applications.

# INTRODUCTION

This work continues the exploration of an unconventional bottom-up gold filling process for robust microfabrication of new device architectures that serve important technical applications.<sup>1-5</sup> The electrodeposition process enables void-free Au filling of recessed trenches and vias on fully metallized patterned substrates followed by self-termination of the growth process without significant deposition, or overburden, on the overlying field. The process efficiently yields dense gold structures that are close to ideal for use as gratings in X-ray interferometry, which is a method for X-ray wave-front-sensing and phase-contrast imaging in one-dimensional<sup>6</sup> as well as twodimensional implementations<sup>7</sup>. As a wave front sensor<sup>8</sup>, hard X-ray interferometry with 2D gratings has found application in optics characterization, optics alignment and focus characterization at X-ray free-electron lasers (XFELs). With femtosecond pulse durations, the rapid evolution of hard XFELs<sup>9,10</sup>, has enabled a wide range of previously impossible dynamical studies of atoms, molecules, clusters, and materials in the physical and life sciences. Talbot interferometers and their variations, such as multilateral shearing interferometers or modified Hartmann mask interferometers use 2D gratings such as chessboard or mesh patterns<sup>7</sup> to measure with high accuracy the phase gradient of the illumination wavefront<sup>11</sup>. The gratings are typically etched in silicon substrates and then filled with high X-ray absorbing materials such as Au<sup>8</sup>.

X-ray phase contrast imaging<sup>12</sup> has found widespread applications ranging from biomedicine to material science and security. For biomedical imaging<sup>13</sup> the technique enables enhanced imaging contrast of low density materials even as it reduces x-ray dose, but gratings appropriate for X-rays hard enough to penetrate tissues (> 30 keV) are needed, with larger area gratings providing for an increased field of view. Sufficient spatial resolution and contrast require dense Au gratings with micrometer or sub-micrometer pitch, features with high aspect ratio (depth/width  $\geq$  50) and increased dimensionality, all of which are addressed herein. The wafer level process that is used enables scale-up, potentially to 300 mm or even 450 mm diameter workpieces, that will greatly mitigate the difficult challenge associated with stitching together smaller gratings as done in recent mammography<sup>14</sup> and chest imaging<sup>15</sup> studies. Within the context of Damascene processing, electrodeposition on fully metallized wafers also offers the possibility of alternative architectures, such as partial filling of trenches with highly conformal deposition of Au<sup>16</sup> or Ir<sup>17</sup> of controlled thickness on the sidewalls. However, only superconformal filling such as the extreme bottom-up version described here enables the formation of void-free metallization of arbitrary complexity. The alternative is more complex through mask plating processes and architectures where a common back plane and nonconducting sidewalls, such as can be obtained, for example, by oxidation of the sidewall surfaces<sup>18,19</sup>, yield analogous filling.

Although gratings fabricated using the bottom-up filling Au electrodeposition process are already being applied to biological imaging<sup>5</sup>, further improvement in grating fabrication calls for a more complete understanding of its function and limits. Deposition in additive-free Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> + Na<sub>2</sub>SO<sub>3</sub> electrolytes is slow and nominally uniform (not accounting for roughness) on all surfaces, i.e., conformal, with the reaction being inhibited by adsorption of sulfite and related Au complexes on the electrode surface. Additives such as Tl<sup>+</sup> and pulse plating can be used to improve

the uniformity and smoothness of the resulting Au film.<sup>20-24</sup> Use of Bi<sup>3+</sup> additive in the processes of interest, in contrast, provides the highly non-linear acceleration and bottom-up feature filling, under appropriate conditions of transport and applied potential (or current), that makes these processes so useful. The behavior is distinct from that seen in other additive-derived superconformal<sup>25-30</sup> and bottom-up filling<sup>31-35</sup> processes, including those for Au<sup>28-30,34,35</sup>. Four important feature filling characteristics of the Bi<sup>3+</sup>-derived filling are: 1) an extended but finite "incubation period" of conformal deposition, 2) subsequent activation of deposition localized to the bottom (i.e., most recessed) surface of recessed features, 3) continuing accelerated deposition and upward propagation of the growth front to yield void-free filling and 4) self-passivation of the active growth front at a defined distance from the feature opening. The duration and detailed evolution of all four stages have been found experimentally to be controlled by electrolyte concentrations and pH, applied potential (and/or current), feature dimensions and convective transport conditions. Correlations between process parameters and feature filling behavior have been established<sup>1-5</sup> for electrolytes including 0.08 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> + 0.64 mol·L<sup>-1</sup> Na<sub>2</sub>SO<sub>3</sub> and 0.16 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> + 0.64 mol·L<sup>-1</sup> Na<sub>2</sub>SO<sub>3</sub> with pH between 8.5 and 10.5. Cyclic voltammetry and chronoamperometry using a rotating disk electrode (RDE) has been used to characterize the impact of  $Bi^{3+}$  concentrations ranging from 1 µmol·L<sup>-1</sup> to 20 µmol·L<sup>-1</sup> on the activation of Au deposition under a variety of conditions. Deposition in patterned substrates has been explored over an analogous range of deposition conditions with Bi<sup>3+</sup> concentrations ranging from 1  $\mu$ mol·L<sup>-1</sup> to 50  $\mu$ mol·L<sup>-1</sup>. Void-free, bottom-up filling was demonstrated in a number of one-dimensional (1D) arrays of trenches: 3  $\mu$ m deep and aspect ratio (depth/width, AR)  $\approx$  1.5; 5.5  $\mu$ m deep AR  $\approx$  8.5; 45  $\mu$ m deep AR  $\approx$  11 and AR  $\approx$  30; 60  $\mu$ m deep AR  $\approx$  40; 85  $\mu$ m deep AR  $\approx$ 56; 100 µm deep AR  $\approx$  38; and 210 µm deep AR  $\approx$  30. The trench widths were nominally equal to

one-half their periodic spacing, i.e., pitch, in all cases.

A robust, quantitative understanding of the feature filling dynamics remains to be established. Empirically, however, the most important aspects are the sustained passive or inhibited deposition that occurs on both the sidewalls of, and the field above, recessed trenches and the highly active deposition that, following the incubation period, concurrently develops on the most recessed surface. A non-monotonic dependence of the passivation of the field on hydrodynamics is also unusual, with faster flow sustaining the field in a passive state for a longer period of time<sup>1</sup>. The above phenomena speak to the importance of the more quiescent environment associated with recessed surface segments and therein are suggestive, perhaps, of a slowly developing depletion gradient; perturbation of pH is the most likely candidate in light of the known increase in the rates of both Au deposition and Bi adsorption with a modest increase in alkalinity. The identity, stoichiometry, kinetics and efficiency of any underlying parasitic reactions remain to be established although the chemistry associated with SO<sub>3</sub><sup>2-</sup> reduction as well as its pK<sub>a</sub> reactivity and surface chemistry of the products are likely involved. Further still, the impact of all the above on the rate of Bi adsorption and its operation as an accelerator remains to be fully examined.

That said, despite filling results that can only be described as remarkable, and even with further optimization of the filling conditions, the range of the bottom-up filling dynamic will have limits. In particular, although deposition on the sidewalls can be orders of magnitude slower than the deposition rate on the active bottom surface, for sufficiently narrow (submicrometer) and high aspect features, cumulative passive deposition increases the aspect ratio to an extent that metal ion depletion induces formation of a key-hole void. "Truncated bottom-up filling", where Au deposition activates on a portion of the upper sidewalls after the start of bottom-up filling but prior to its completion, is another source of void-entrapment.

Herein the bottom-up Au filling of gratings is explored in substrates patterned with two different geometries. A novel two-dimensional (2D) array of recessed vias having nominally square cross-section and arranged in a "chessboard" geometry as shown schematically in **Fig. 1** is examined for the first time. The filling of trench arrays, the focus of previous studies, is also examined further. One array has approximately 66  $\mu$ m deep trenches of aspect ratio (AR)  $\approx$  50. The other array has approximately 60  $\mu$ m deep trenches of nominal AR  $\approx$  60; the effective AR for void-free filling of these latter trenches exceeds 65 based on narrowing in the upper region of the trenches in their fabrication. Both trench arrays are deeper than any trench arrays of 2  $\mu$ m pitch (or smaller) that have been filled void-free to date, and both the nominal and effective AR of the latter array are higher than any previously filled void-free. Given that 0.16 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> containing 50  $\mu$ mol·L<sup>-1</sup> Bi<sup>3+</sup> concentrations up to 20  $\mu$ mol·L<sup>-1</sup>,<sup>4,5</sup> deposition in these even more challenging features was additionally explored in an electrolyte with a yet higher gold concentration of 0.32 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> containing 50  $\mu$ mol·L<sup>-1</sup> Bi<sup>3+</sup>.

#### GOLD DEPOSITION

#### **Experimental Details**

High-aspect-ratio, small-pitch gratings in Si substrates can be realized with etching methods including deep reactive ion etching<sup>36,37</sup> and metal assisted chemical etching<sup>38</sup>. The former process, detailed previously<sup>36</sup>, was used for the etching of the linear gratings in Si substrates used here. Fabrication of the chessboard gratings started with evaporation of a 100 nm thick Cr layer on one side of a 250 µm thick double-side polished Silicon (001) wafer. Subsequently, a 400 nm thick layer of poly(methyl methacrylate (PMMA 950k) electron-beam resist, 4 % mass fraction in ethyl

lactate, AR-P679.04, Allresist GmbH) was spin-coated at 2000 rpm ( $4000\pi$  rad·min<sup>-1</sup>) for 1 min and baked at 175 °C for 5 min on a hot plate. Areas 15 mm × 15 mm were patterned with chessboards having 2 µm period and square openings 800 nm wide using an electron beam direct write lithography system Raith EBPG5000Plus operated at 100 kV acceleration voltage. The base exposure dose was set to 850 µC·cm<sup>-2</sup>. Dose correction of the pattern was calculated using BEAMER software (GenISys GmbH) to correct for the proximity effect and ensure constant feature size across the field. Development of the exposed wafer was performed using a mixture of methyl isobutyl ketone (MIBK) and isopropyl alcohol (IPA) (ratio 1:3 by volume) for 25 s and stopped by rinsing with IPA for 30 s.

The chessboard pattern was transferred into the Cr film by reactive ion etching (RIE) in a  $Cl_2/CO_2$  atmosphere (flow rates 50 sccm/20 sccm) using a parallel plate etcher from BMP. The resulting hard metal mask for Si etching had 900 nm × 900 nm square openings. The reduced size of the square openings maintained continuous Si walls across the chessboard pattern despite modest lateral etching.

Etching of both the chessboard and linear patterns was performed in an Oxford PlasmaLab 100 ICP system. The etching optimization has also been previously detailed<sup>36</sup>. Convection during the process is poor in both patterns due to the small lateral dimensions, limiting the etching rate particularly after the ratio of depth to width exceeds approximately 10. Chamber pressures of 15 mTorr (2 Pa) for the linear specimens and 20 mTorr (2.7 Pa) for the chess board specimens were found to yield transport of etchants and byproducts inside the narrow features consistent with uniform Si etching through the depth of the features. The Teflon-like polymers that accumulated on the sidewalls during the etching process were removed by a follow-up plasma treatment using an SF<sub>6</sub>/O<sub>2</sub> mixture as etchant gas in order to avoid delamination of subsequent metal coatings. The

trench arrays include cross-bars that bridge the trenches to reduce sidewall displacement during the Au deposition process. They are spaced 100 µm apart, their locations staggered by half a period between adjacent trenches. For exploratory filling studies, sacrificial wafers were cleaved into fragments having patterned regions 3 mm wide by 11 mm to 12 mm long that were imaged after deposition. Larger arrays, including patterned 100 mm wafers, were fabricated for X-ray interferometry and wavefront sensing.

A conductive seed layer for electroplating on the Si trench arrays was formed through conformal growth of a Pt/Al<sub>2</sub>O<sub>3</sub> bilayer (20 nm thick platinum on 5 nm thick Al<sub>2</sub>O<sub>3</sub>) by atomic layer deposition (ALD) followed by conformal growth of 50 nm to 100 nm thick Au layer using electrochemical deposition in a cyanide electrolyte. The via arrays also have a Pt ALD layer, 20 nm thick. However, the overlying Au (on Ti for adhesion) layer was evaporated at near-normal incidence to the wafers, yielding approximately 70 nm thick Au on 20 nm thick Ti on the field and feature bottoms with only minimal, discontinuous coverage on the cusps of the scalloped sidewalls from the Bosch process cycles. Electrical conductivity over the entire surface is ensured by the highly conformal Pt layer; the Au layer improves electrical conduction across the specimen and serves as a seed layer, thereby removing the nucleation barrier otherwise associated with Au electrodeposition on Pt. Electrical contact for the superconformal Au deposition was made either to the front surface or to both the front and rear surfaces of the patterned specimens without noticeable difference in filling.

The chessboard patterns shown schematically in **Fig. 1** have vias that are approximately 23  $\mu$ m deep, the width of their nominally square cross sections being approximately one-half the 2  $\mu$ m pitch with modest rounding of the corners that prevents overlap. Images of a cleaved specimen showing Au filled vias, details discussed later, are shown as well. Filling is also examined in arrays

of 66  $\mu$ m deep trenches that are 1.3  $\mu$ m wide (AR  $\approx$  50) and 60  $\mu$ m deep trenches that are nominally 1.0  $\mu$ m wide (AR  $\approx$  60), but effectively 0.9  $\mu$ m wide (AR > 65), both of 2.0  $\mu$ m pitch.

The bottom-up Au electrodeposition was conducted in 40 mL to 400 mL of electrolyte, as convenient. The electrolytes included 0.32 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> (Technic Gold 25-F replenisher concentrate), diluted using 18 M $\Omega$ ·cm water as indicated, and 0.64 mol·L<sup>-1</sup> Na<sub>2</sub>SO<sub>3</sub>. The pH of the electrolytes, in the range 9.7 to 9.8 as mixed, was adjusted down using  $H_2SO_4$  (prediluted in distilled water sufficiently to avoid gold precipitation) and up using NaOH (dissolved in distilled water for greater control). The Bi<sup>3+</sup> additive was introduced by anodic dissolution of 99.999 mass % Bi metal, the possibility of parasitic oxidative processes making stated concentrations upper bounds. Deposition on wafer fragments was conducted with the specimen either rotating about one end from a Pt spindle, the patterned surfaces of the specimens parallel to the flow direction in the electrolyte (i.e., helicopter blade) facing upward or downward, or suspended and rotated about the long vertical axis of the rectangular specimens, as indicated for each specimen. The suspended specimen geometry has a complicated flow field but deposition can be limited to the patterned region of the substrate alone. The helicopter blade geometry provides better defined shear flow but the slot in the spindle in which the substrates are clamped, being immersed in the electrolyte with the specimen, also experiences Au deposition. To avoid trapping of air bubbles upon insertion in the electrolyte, the via arrays were first evacuated to < 0.1 torr (10 Pa) using a mechanical pump then backfilled with distilled water. After immersion in the electrolyte they were rotated for several minutes under open circuit conditions before the start of deposition to allow mixing of electrolyte into the water filled features.

Deposition in the unseparated cell was accompanied by acidification of the electrolyte, most likely associated with oxidation of sulfite to sulfate at the Pt anode. Its impact was significant only during extended feature filling experiments. Accordingly, the electrolyte pH was checked between specimens and, prior to deviation below 0.2 pH units of the specified value, was adjusted back to the starting value by addition of NaOH. Potentials in experiments on planar as well as patterned substrates were measured relative to a Hg/Hg<sub>2</sub>SO<sub>4</sub>/saturated K<sub>2</sub>SO<sub>4</sub> reference electrode (SSE). For the voltammetric measurements, in which the observed currents reached several tens of milliamperes in some cases, iR compensation was used to partially correct (85 %) for ohmic losses due to current flow across the 4  $\Omega$  measured resistance between the working electrode contact and the reference electrode. No attempt was made to compensate for potential drop during feature filling experiments given deposition currents that were typically below 1 mA.

Procedures for cross-sectioning specimens for scanning electron microscope (SEM) imaging have been detailed previously.<sup>1-5</sup> That said, cross-sectioning of via arrays poses additional challenges that are not encountered in studies with trenches. As indicated in **Fig. 1a**, misalignment during sectioning is possible (indeed, it was generally the default case). With small nonzero deviation of the tilt angle  $\psi$  away from a row of vias, the specimen exhibits via cross-sections that pass systematically through the via thickness *w*, the pattern repeating every  $1/\sin \psi$  vias along the section as the cross-section deviates from one row of vias to the next. This systematic sectioning of the vias is actually useful and effective for capturing the narrow unfilled region that can form when significant sub-conformal sidewall deposition occurs. Nonzero value of the tilt angle  $\phi$ , on the other hand, is problematic because a via that is sectioned along the midline at its top is not sectioned along its midline at its bottom. For angular deviation such that  $\tan \phi > w/2h$ , a section that goes through the midline at the top of the via will exit the sidewall of the via rather than reach the via bottom. Because the vias are one half cycle out of phase in adjacent rows, this manifests in portions of the cross-section having the upper region of vias in one row with the lower region of vias from the adjacent row interleaved between them. For the 1  $\mu$ m wide and 23  $\mu$ m deep vias in this study, the angular deviation  $\phi$  at which this occurs is only a little less than 1.25°. Neither misalignment angle poses a problem in cross-sectioning of trenches, aside from the more trivial apparent modification of dimensions.

### **Deposition on Planar Substrates**

Electroanalytical measurements with an RDE are used in combination with feature filling experiments on small patterned specimens to facilitate identification of conditions compatible with void-free processing in the Bi<sup>3+</sup> containing Au electrolyte. Cyclic voltammograms on the Au coated RDE in 0.32 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> + 0.64 mol·L<sup>-1</sup> Na<sub>2</sub>SO<sub>3</sub> electrolyte containing different  $Bi^{3+}$  concentrations are shown in Fig. 2. The impact of  $Bi^{3+}$  concentration, with rotation rate of 1600 rpm defining transport, is summarized in Fig. 2a. The Au deposition rate and voltammetric hysteresis both increase with additive concentration. The slight hysteresis in additive-free electrolyte (Fig. 2b) is likely associated with increase of surface area through roughening of the RDE surface, which darkened slightly after completion of the cycle. However, the bright surfaces observed after cycling in the presence of Bi<sup>3+</sup> indicate the much greater hysteresis in these cases is in fact due to acceleration of the deposition kinetics. The impact of hydrodynamics (RDE rotation rate) on the rate of metal deposition is presented for a range of additive concentrations in Figs. 2c-2h. The voltammograms are qualitatively similar to those obtained from electrolytes with lower Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> concentration, where Au deposition current and voltammetric hysteresis also increased with the Bi<sup>3+</sup> concentration. Cumulative increase of the deposition rate on activated regions, as Bi<sup>3+</sup> coverage increases, is the origin of both acceleration and hysteresis. Interestingly, dependence of the deposition rate on transport inverts between the activation and passivation

branches. More precisely, higher rotation rate yields more rapid rise of the current density when scanning negative of -1.0 V but more rapid fall-off of the current density on the return scan positive of -1.0 V. These effects are most evident in the voltammograms for higher Bi<sup>3+</sup> concentrations. The dependence on transport for each of the Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> concentrations in the electrolytes is summarized in **Fig. 3a-c**. The current density at the switching potential essentially doubles with fourfold increase of RDE rotation rate  $\omega$  in a manner that is consistent with the Levich equation for the diffusion limiting current  $i_L$ , where n is number of equivalents, *F* is Faraday's constant, *D* the diffusion coefficient, v is the kinematic viscosity,  $\omega$  the angular velocity in rad·s<sup>-1</sup> (=  $2\pi$ f, where f is revolutions per second) and *C* is the Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> concentration:

$$i_L = 0.620nFAD^{\frac{2}{3}}v^{-\frac{1}{6}}\omega^{\frac{1}{2}}C$$
[1]

Consistent with the behavior in **Fig. 2** for  $0.32 \text{ mol}\cdot\text{L}^{-1}$  Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub>, deposition is seen to suppress on the return scan more rapidly at higher rotation rate for each of the Au concentrations; the effect is even more substantial when the voltammograms are scaled by their limiting currents (i.e., Levich Koutecky), as previously shown<sup>1</sup> for  $0.08 \text{ mol}\cdot\text{L}^{-1}$  Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub>. When the same results are grouped by the RDE rotation rate to allow comparison of the impact of metal ion concentration, as in **Fig. 3d-f**, acceleration manifests at progressively more negative potential, indicating slower accelerator adsorption and/or activation, with higher Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> concentration. In addition, the limiting currents less than double as the Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> concentration doubles from 0.08 mol·L<sup>-1</sup> to 0.16 mol·L<sup>-1</sup> and then to 0.32 mol·L<sup>-1</sup>, as would be anticipated for simple scaling with the Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> concentration *C*. The deviation is clear for each of the RDE rotation rates examined, although the fractional deviation is greatest upon the increase from intermediate concentration to highest concentration. It remains to be determined whether this reflects variation in diffusion coefficient or kinematic viscosity between the different electrolytes or rather the impact of an increased role of migration forces with the increased Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub>/Na<sub>2</sub>SO<sub>3</sub> ratio whereby a decrease in transport of the triply charge Au(SO<sub>3</sub>)<sub>2</sub><sup>3-</sup> anionic complex to the negatively charged electrode surface might be anticipated. Regardless of its origin, the result suggests that improvement of filling noted upon increase to the intermediate Au concentration<sup>4,5</sup> may be less significant upon increase to the highest concentration particularly if the behavior extends to more positive potentials and lower pH electrolytes used for filling the highest aspect ratio features, *vide infra*. Going further still, bottom-up Au feature filling in the more concentrated electrolyte may even be degraded if the active deposition rate on the bottom surface scales in this sub-linear manner with concentration while the passive deposition rate on the sidewalls scales linearly.

Conditions for which deposition on the free surface remains suppressed while filling proceeds within the most recessed regions of features have been explored experimentally in electrolytes with Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> concentration of 0.16 mol·L<sup>-1</sup> and below. Faster substrate rotation as well as more positive deposition potentials were found to support longer surface passivation on both RDE and patterned substrates.<sup>19,21</sup> Building upon the prior results, chronoamperometry is used to explore the impact of a higher Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> concentration on the deposition process with particular attention given to breakdown of the passive state at potentials positive of -0.96 V. As shown in **Fig. 4** the transients exhibit a period of slow, passive deposition before activation of deposition manifests as a rising current. This incubation period increases monotonically from tens of seconds to thousands of seconds as the deposition potential is made more positive. Significantly, increasing the rotation rate from 25 rpm to 300 rpm *increases* it from approximately 80 s to 60 s at -0.96 V. The cross-over between inhibition and acceleration occurs at -0.92 V; i.e., an increased rotation rate extends the incubation period at more positive potentials while shortening it at more negative

potentials. Interestingly, cross-over of the impact of rotation rate in lower concentration electrolytes also occurred at a potential between -0.90 V and -0.95 V.<sup>1</sup> Analogous lengthening of the incubation period with more positive potential was also observed with more dilute electrolyte and timescales were similar for electrolyte with a similar pH while higher pH values substantially accelerated the activation.<sup>4</sup> The complex dependence of the incubation period on both potential and rotation rate in electrolytes with lower Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> concentration has been correlated with closely allied studies of Bi adsorption on planar surfaces by X-ray photoelectron measurements.<sup>2-</sup>

#### Deposition in Via Arrays

Given the similar electroanalytical response on planar electrodes during Au deposition with all three Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> concentrations, analogous behavior is anticipated for deposition on patterned substrates. Furthermore, since the bottom-up filling evolution is essentially one dimensional, void-free Au filling of high aspect ratio features in electrolyte with 0.32 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub>, hitherto unexplored, is anticipated to occur. Indeed, there is also reasonable expectation that the underlying mechanism will function in features of arbitrary cross section and arrangement. Filling of nominally square vias arranged in the chessboard array pattern (see **Fig. 1**) is shown as a function of applied potential in **Fig. 5**. As with trench filling that transits from subconformal deposition to bottom-up growth with the use of more positive deposition potentials, via filling improves as the potential shifts positive: deposition from the via bottoms is minimal from -0.84 V to -0.80 V, slight at -0.78 V, substantial at -0.76 V and complete at -0.74 V. Thus, in keeping with the filling of trenches, as the potential shifts positive via filling exhibits: voided fill resulting from subconformal deposition on the begins but is truncated by activation of deposition on the

upper sidewalls (which entraps a void over the bottom-up deposit) and void-free bottom-up filling. The via filling also exhibits self-termination of the bottom-up growth as the growth front approaches the upper surface, the distance remaining unfilled depending on the process conditions. The specimens shown were rotating at 600 rpm during deposition; filling at 300 rpm differed only in slightly higher filling (i.e., passivation) and increased deposition on the field at -0.84 V. The self-termination of bottom-up growth manifests the balance between activation that starts at the location most recessed from the via opening and passivation that is maintained near the surface and represents a further similarity with Bi stimulated bottom-up filling seen previously in trenches.

Truncated bottom-up filling occurs when bridging of the deposits follows activation of the sidewalls at the location effectively marked by the top of the principle occluded void, thereby preventing complete bottom-up filling. Examination of the higher magnification images in **Fig. 5** shows that this sidewall activation shifts farther down the vias (i.e., farther from the via openings) at more positive potential. The nonconformal filling above this location, especially significant in the specimen filled at -0.76 V, reflects bottom-up filling from the bridge and/or geometrical leveling through conformal deposition that occurs subsequent to formation of the bridge.

Higher magnification images of the specimen filled at -0.78 V in **Fig. 6** exhibit both horizontal and v-shaped growth fronts over the bridged deposit as well as enhanced deposit thickness at the via bottoms reflecting the initiation of bottom-up filling prior to its truncation by the breakout of sidewall deposition further up the via. Filling approximately 1  $\mu$ m above the tiny voids reflects geometrical leveling from subsequent conformal deposition of perhaps one-tenth this amount given the  $\approx 6^{\circ}$  internal half angle of the v-notch. Higher magnification images of the specimen filled at -0.76 V in the same figure show the flat bottoms of the occluded voids. Located roughly halfway up the vias, these mark the locations where bottom-up filling was halted by formation of the transport-blocking bridges at the upper ends of the voids. Grain boundaries that formed as the bottom-up deposition propagated rapidly up the central region past the accumulated sidewall deposits are seen along with topographical contrast due to unintentional, artifactual beveling of the Au deposits by the ion beam used for polishing prior to imaging. The image of the specimen filled at -0.74 V highlights an analogous grain boundary running down from the left corner of the passivated central growth front. Microstructure that suggests grain growth and/or recrystallization from the sidewalls that occurred subsequent to filling is visible farther down on the righthand side. Significantly, the bottom-up nature of the process enables void-free filling regardless of the presence of scalloped surfaces from the Bosch etching process that are particularly evident just below the field.

The corresponding current density and cumulative deposition charge transients, normalized by the projected area of the patterned surface of the specimens, i.e., ignoring the sidewalls, are shown in **Fig. 7**. Substantial increase of current from the start of deposition in all the transients reflects Au nucleation and passive deposition on the poorly Au covered, Pt coated via sidewalls. At potentials of -0.76 V and negative it is evident from consideration of the associated specimens in **Figs. 5** and **6** that the current also increases due to Bi<sup>3+</sup>-derived activation of the upper sidewalls; there is no obvious demarcation in the current or charge transients that distinguishes the initial nucleation and subsequent uniform passive growth on the sidewall surfaces from the more localized deposition associated with the bridging. The rising current transient at -0.76 V evidently also convolves a short period of bottom-up filling. In contrast, at -0.74 V the current rises toward a plateau, suggesting development of a uniform Au coating and constant passive deposition rate on the sidewalls and bottom, until a second transient increase of current at approximately 12 h marks the onset of bottom-up filling. The rising current associated with progress in upward filling

in the vias is somewhat more gradual than the subsequent decrease of current that marks the final resumption of passivation. As the bottom-up growth front advances the metal ion depletion gradient becomes steeper, likely contributing to the acceleration. Variation in the onset of activation from via-to-via is evident in the sectioned specimens and is attributed to non-uniform etching of the via bottoms. The dispersion likely also contributes to an increase in the duration of both rise and fall of the current transients. In contrast, the current traces for deposition at more negative potentials decline precipitously as the impinging sidewalls remove surface area in a noncontinuous manner. The sharp transition indicates concurrent failure that is consistent with the more uniform growth front positions and via dimensions in the upper regions where the sidewall activation occurs. The measured deposition currents often remain significant following passivation, more so at more negative potentials, despite experimentally clear passivation in the patterned features; stray deposition on unmasked sections of the substrate holder and specimen is appreciable. Given the relationship of deposition charge and current, the slopes of the charge transients increase/decrease with the currents. Kinks in the charge transients when the slope decreases upon passivation are clear for the specimens with a more extended period of postpassivation deposition. The deposition charge at this passivation-induced kink increases at more positive potentials, consistent with increased Au in the vias and improved filling, albeit with contributions from the holder and field leading to values in excess of that anticipated for via filling. For 100 % efficient deposition, the charge per area  $Q_A$  associated with filling the pattern is obtained from the molar volume of the filling metal  $\Omega_m$ , the fraction of the patterned area that is recessed f, the feature depth h, the deposition charge n and Faraday's constant  $F = 96485 \text{ C} \cdot \text{mol}^{-1}$  using

$$Q_A = \frac{nFfh}{\Omega_m} \tag{1}$$

For 23  $\mu$ m deep vias composing one-half the patterned surface, a deposition charge equivalence of 1 for gold sulfite Au(SO<sub>3</sub>)<sub>2</sub><sup>3-</sup> that liberates two sulfite (SO<sub>3</sub>)<sup>-2</sup> ligands upon Au deposition and the 10.2 cm<sup>3</sup>·mol<sup>-1</sup> molar volume of Au, gives an anticipated filling charge of 10.9 C·cm<sup>-2</sup> that is substantially exceeded by the measured charge at the passivation kinks for both -0.76 V and -0.74 V in **Fig. 7b** due to the parasitic deposition described above.

The aspect ratio of these vias is lower than that of trenches that were previously filled in  $Bi^{3+}$ containing electrolyte of the intermediate 0.16 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> concentration. Accordingly, filling of via arrays using electrolyte with this lower gold concentration containing the same 50 µmol·L<sup>-1</sup> Bi<sup>3+</sup> concentration was examined. Expecting that the specific rate of transport over the features should not substantially impact the bottom-up filling dynamic in these relatively high aspect ratio features, a rotation rate of only 200 rpm was used. The patterned wafer fragments were, furthermore, suspended and rotated about a vertical axis (the rotation axis being parallel to the major axis in the plane of the rectangular specimen), with the advantage that the contact region and holder were maintained outside the electrolyte. With deposition constrained to the patterned region of the specimen, thereby avoiding parasitic deposition detailed earlier, the transients provide a more faithful representation of the deposition underway within the recessed features.

A flat and horizontal growth front characteristic of the bottom-up filling process is seen in the sectioned vias in **Fig. 8**; microstructure that marks propagation of this front past the conformal sidewall deposits, particularly the grain boundaries formed along the conformal deposits on the sidewalls above, is clear in the higher magnification images. Void-free filling is obtained not only at -0.74 V, as with the 0.32 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> electrolyte, but also at -0.76 V. Because fluid flow over the surface is generally reduced, passivation of the bottom-up growth front occurs at a somewhat less recessed position than in **Fig. 5** at the same potentials. Specimens filled at -0.78 V

for different deposition times are shown in **Fig. 9**. They capture the modest evolution of fill height in the final stages of deceleration and leveling out of the upward growth that occurs in the upper portion of the vias after truncation of earlier bottom-up growth from the via *bottom*. As per the associated current and charge transients in Fig. 10 the specimens represent filling at the maximum current, the end of the passivation transient and beyond it, respectively. For the -0.74 V potential, the cross-sections also shown in Fig. 9 highlight some additional features of the bottom-up nature of the filling process. These include substantial variation in the deposit height in the earlier stages of filling, due at least in part to variation of the via shapes visible toward their bottoms, followed by attenuation of the variation as the growth process terminates. The corresponding transients are also included in **Fig. 10**. The rising current density when the partially filled specimen was pulled from the electrolyte at 6.7 h indicates that increasing transport, e.g., steeper metal ion depletion gradient, correlates with accelerating deposition on the upward moving bottom deposit. The steady, nonzero currents after filling passivates in Fig. 10a, increasing in magnitude at more negative potential (seen also in the linear dependence of charge on time after the passivation kink in Fig. 10b) reflect passive deposition rates on what has essentially become a planar surface.

As with the via filling itself, the associated transients exhibit features analogous to those observed with the higher concentration electrolyte. These include current rising substantially over the first several hours as the Pt sidewalls are covered with gold and, where bottom-up filling occurs, a plateau preceding the acceleration (and deceleration) of the activated bottom surface. Here, however, bottom-up filling is obtained at both -0.74 V and -0.76 V and a modest but steady *decrease* of current is observed prior to the current rise at 4.5 h for -0.76 V and 6 h or 6.5 h for -0.74 V that marks bottom-up filling. This decline, highlighted in an additional plot of current transients on substantially larger patterned specimens in **Fig. 10c**, is attributed to the decreasing

area upon which the passive deposition occurs as the via radius decreases with the conformal deposition. It is also noted that time-dependent roughness from Au nucleation, growth and coalescence on the poorly Au-seeded sidewalls may also play a role in the evolution of the transient. The absence of this trend in **Fig. 7** most likely reflects masking of this effect by parastici deposition on the specimen holder. This decline seen with the vias contrasts with the flat plateau that is observed to precede the onset of bottom-up filling in high aspect ratio trench arrays and which reflects surface area that is essentially unchanged by conformal deposition.<sup>5</sup>

There is also a substantial difference in the time required for void-free bottom-up via filling in the two electrolytes; bottom-up filling *begins* at 6 h or 6.5 h at -0.74 V in the 0.16 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> electrolyte (**Fig. 10a**) versus at 12 h at the same potential in the 0.32 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> electrolyte (**Fig. 7a**). There is further improvement in filling time with the lower Au concentration through the modestly expanded processing window, with void-free filling at -0.76 V already *completed* by 6.7 h (**Fig. 8**). It is believed that the difference in incubation times is inherent to the electrolyte-additive system interactions within the vias; hydrodynamic differences likely underlie little, if any, of the difference, given that 300 rpm and 600 rpm yielded similar filling with the 0.32 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> electrolyte (as noted with **Fig. 5**) and uniform filling was obtained across the substrates despite the irregular convection with the 0.16 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> electrolyte (in **Fig. 8**). It is likely that extension of the window for void-free filling to -0.76 V is related to the shortened incubation period and lower passive deposition rate in the 0.16 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> electrolyte, given that both reduce the cumulative thickness of the sidewall deposits that are detrimental to void-free filling.

Somewhat lower current densities in the lower concentration electrolyte (Fig. 10a versus Fig.7a) reflect elimination of deposition within the holder as well as decreased passive deposition rate

on the field in the lower concentration electrolyte. Even at their peaks, the current densities associated with void-free filling, at -0.74 V with 0.32 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> as well as -0.76 V and -0.74 V with 0.16 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub>, are seen to reach no more than -0.7 mA·cm<sup>-2</sup>. This would seem well below the transport limit considering the corresponding values of -34 mA·cm<sup>-2</sup> for 0.32 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> and -25 mA·cm<sup>-2</sup> for 0.16 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> on a conventional RDE at 400 rpm (**Fig. 3**). However, the transport limit is likely more restrictive than these values suggest. In particular, the local current density relevant to bottom-up growth is at least 8× higher than the transient indicates (i.e., approximately -6 mA·cm<sup>-2</sup>) because via coverage is less than one-half the projected area and bottom-up filling is confined to less than one-quarter the via area (one-half the via diameter, **Figs. 5** and **8**). Diffusion limited current across the combined depth of the boundary layer and the 23 µm deep via will also be below the transport limited values measured for the rotation-rate dependent boundary layer thickness. The rising current observed during active bottom-up filling certainly suggests steepening of the metal ion gradient plays a role as the vias fill.

As a last point, larger charges upon passivation at -0.74 V and -0.76 V (i.e., at the passivation kinks) in **Fig. 7b** as compared to those in **Fig. 10b** suggest undesired, parasitic deposition on the immersed specimen holder is indeed contributing significantly to the former values. Deposition charges upon passivation in **Fig. 10b** that are closer to the 10.9  $C \cdot cm^{-2}$  value expected for void-free filling also suggest improved accuracy of the measurement with the contact zone and holder removed from the electrolyte. Significantly, the early behavior noted in **Fig. 10c**, matching that **Fig. 10a**, indicates that the evolution of filling is not altered through use of the suspended geometry.

# Deposition in Trench Arrays

As described earlier, filling of gratings composed of 1D trench arrays has been previously demonstrated in trenches up to AR  $\approx$  56 at a pitch of 3 µm. Given the final surface profile, filling of the highest aspect ratio trenches was accompanied by the suggestion that this was not the limit of the bottom-up Au filling process.<sup>5</sup> Here, filling of smaller pitch trenches that are approximately 66 µm deep and nominally 1.3 µm wide (AR  $\approx$  50) is examined in 0.16 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> + 0.64 mol·L<sup>-1</sup> Na<sub>2</sub>SO<sub>3</sub> electrolyte containing 50 µmol·L<sup>-1</sup> Bi<sup>3+</sup> as a function of applied potential. The wafer specimens were again rotated about the vertical axis at 200 rpm with the electrode contact outside the electrolyte to avoid extraneous current. As shown in **Fig. 11**, filling again transitions from subconformal to truncated bottom-up to complete bottom-up as the potential is shifted to more positive values. The usual trend of increasing passivation depth at more positive potential is, in this case, altered by deposition at -0.74 V that continued long past passivation. Shorter deposition in a specimen at -0.76 V is shown in **Fig. 12**; the extremely high aspect ratio of its unfilled center foreshadows the coming failure despite the start of bottom-up filling.

Current and charge transients associated with specimens including those in **Figs. 11** and **12** are shown in **Fig. 13**. Modest differences in the current transients at a given potential, including the variation in incubation times, due in great part to the very modest pH variation, did not alter the filling behavior; the specimens all exhibited void-free fill at -0.74 V and some degree of voided fill at -0.76 V in accord with the specimens imaged in **Fig. 11**. It is noteworthy that over the first 3 h of the transients in **Fig. 13a** the current little more than doubles from the initial value on the conformal Au seed layer. This contrasts with the order of magnitude increase of current during the first 3.5 h of conformal deposition at -0.74 V on the via arrays (**Fig. 10**) where nucleation and growth of Au on the poorly Au coated, Pt seeded sidewalls limits the earliest response. The

subsequent current plateau for void-free filling at -0.74 V extends to the start of bottom-up filling at 5.5 h or 6.5 h. Consistent with conformal deposition in the trenches it is essentially flat. Deposition being limited to the patterned substrate, the values of deposition charge at passivation (i.e., the kink) in **Fig. 13b** are not inconsistent with the expected value of 40.6 C·cm<sup>-2</sup>, particularly in light of the incomplete pattern etching in the lower region of the trenches evident in the imaged specimens. The especially low value at -0.78 V reflects the substantial voiding as well.

Importantly, deposition in the conformally Au seeded trenches follows the same sequence of events, and exhibits the same trends, that it does in the vias where the Au seed was incomplete on the sidewalls but uniform on the bottom surface (and field): an incubation period followed by bottom-up filling that improves at more positive potentials followed by passivation. Resilience regarding the nature (and quality) of the initial seed layer is reasonable given the conformal Au layer that deposits on all surfaces during the incubation period as well as earlier demonstrations of bottom-up Au filling of trenches with both uniform and non-uniform Au seed layers. Indeed, even substrates having just the Pt seed layer lacking any Au overlayer exhibit analogous bottom-up void-free filling at -0.74 V. However, Au deposition transients on Pt seeded substrates and on conformally Au seeded substrates filled at -0.74 V, contrasted in **Fig. 13c** and **13d**, show that filling takes far longer in the absence of the Au seed. Acceleration of the bottom-up deposition occurs only after more than 8 h of passive deposition that gives rise to almost negligible deposition charge, effectively demonstrating the importance and utility of the nucleation and coalescence of a Au seed layer on the Pt prior to commencement of the bottom-up Au filling dynamic.

Trenches that are 60  $\mu$ m deep and have the same 2.0  $\mu$ m pitch with a nominal 1.0  $\mu$ m width (AR = 60) filled in the same 0.16 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> + 0.64 mol·L<sup>-1</sup> Na<sub>2</sub>SO<sub>3</sub> electrolyte containing 50  $\mu$ mol·L<sup>-1</sup> Bi<sup>3+</sup> are shown in **Fig. 14**. Significantly, the high magnification images

reveal the minimum width is 0.9 µm in the upper quarter of the trenches, so that the effective aspect ratio for void-free filling exceeds 65. The same trend of improved filling at more positive potential is observed: almost entirely conformal voided deposition at -0.76 V, a narrow central column in the microstructure and final growth profile from marginal bottom-up fill at -0.74 V, and a broader area of bottom-up filling with substantially reduced sidewall deposition at -0.72 V. The associated current transients in Fig. 15a exhibit plateau values that increase in magnitude from -0.3 mA·cm<sup>-2</sup> at -0.72 V to -0.5 mA·cm<sup>-2</sup> at -0.74 V as well as a fairly broad peak of -0.8 mA·cm<sup>-2</sup> at -0.76 V, which together suggest potential dependent passive deposition rates. The deposition charge associated with this period of conformal deposition, upon passivation with voiding at 9 h for -0.76 V as well as at the kinks recording significant activation at 10 h for -0.74 V and 12 h for -0.72 V in Fig. 15b decreases from 20 C·cm<sup>-2</sup> to approximately 15 C·cm<sup>-2</sup> then 12 C·cm<sup>-2</sup> as the potential goes more positive, consistent with the decreasing thickness of the conformal sidewall deposits in Fig. 14. The sidewall deposits are also consistent with those in Fig. 11 and in the modestly deeper vias of Figs. 5 and 8 at the same potentials. The conformal deposition is reflected in the charge remaining for bottom-up filling (i.e., after the activation kink in the deposition charge transients). Deposition at -0.74 V yields an incremental charge of  $\approx 7 \text{ C} \cdot \text{cm}^{-2}$  from activation through passivation while deposition at -0.72 V yields a larger  $\approx 10 \text{ C} \cdot \text{cm}^{-2}$  charge increment, consistent with the broader bottom-up filling profile although both overestimate the bottom-up filling component given that conformal deposition continues on the sidewalls of the unfilled height. Decreasing current on the plateaus at -0.74 V and -0.72 V likely reflects loss of surface area due to limited voiding observed near the cross-bars (not shown). Significantly, the comparatively tight distribution of the transients in **Fig. 15** results from control of electrolyte pH to better than 0.02 units from the 9.00 target value.

The high aspect ratio trenches and vias filled here make clear the ability of Bi-derived bottomup gold filling processes to deliver void-free gold filling of recessed features having a variety of geometries. Although the processes become more constrained as the feature width decreases and aspect ratio increases, the limits remain to be determined even for 2 µm pitch features despite the remarkable results just demonstrated. Measurements on RDE suggest interesting effects going well beyond the recognized acceleration of Au deposition provided by Bi<sup>3+</sup>. Some of these, such as enhanced suppression at faster rotation rate, have been described and explored in earlier iterations of this effort. Others, such as trends of plateau currents with potential and geometry-dependent behaviors, are made clear for the first time through improved control of the immersed specimen geometry and electrolyte pH. Understanding the significance of these observations will ultimately require measurements that properly assay the nature and evolution of localized chemistry associated with activation of the surface and a meaningful evaluation of the associated phase transition kinetics.

# X-ray interferometric imaging experiments

The performance of 1D-gratings was tested with an X-ray grating interferometer setup implemented at TOMCAT, Paul Scherrer Institute. The setup consisted of a microfocus X-ray source (Hamamatsu Photonics, model L10101) and a Dectris Eiger R 1M photon detector with a pixel size of 75  $\mu$ m. The X-ray source was operated with a tube voltage of 42 kV and a current of 200  $\mu$ A, providing a source size of 10  $\mu$ m.

The interferometer was set up in Talbot-Lau configuration, with gratings G0, G1 and G2 placed between the X-ray source and the detector, as shown in **Fig. 16**. Experiments measured the visibility<sup>39</sup> of the X-ray interferometer, a performance metric for grating interferometers that

captures the optical properties of G0 and G2. Denser, more uniform gold fillings is reflected in higher, spatially uniform values of visibility.

Design energy of 20 keV and Talbot order 9 were chosen for the visibility tests. The phase shift grating G1 was manufactured from silicon with unfilled trenches 25 µm deep, providing a phase shift of  $\pi$  at the given energy. The absorption gratings G0 and G2 had bottom-up Au filled trenches that were 60  $\mu$ m deep. All the gratings – G0, G1 and G2 – had a pitch of 2  $\mu$ m and a duty cycle of 0.5 (1  $\mu$ m wide trenches). The visibility was measured using a phase stepping technique<sup>6</sup> where G2 was systematically translated in the plane of the grating perpendicular to the Au line structures with data acquired at each step; in this study G2 was moved a total of 5 steps over one grating period (0.4  $\mu$ m per step). The acquired map of visibility across the measurement area and the histogram of the spatially varying values are seen in **Fig. 17**. A peak visibility of  $\approx 21$  % was achieved, which is considered indicative of a good quality grating<sup>39</sup>. The visibility drops rapidly toward the left and right edges of the map because the high aspect ratio (60) Au filled trenches in the planar gratings are progressively more misaligned from the divergent X-ray beam generated by the laboratory source farther from the central axis of the system (see Fig. 16). The associated increase of absorption toward the edges of the G2 grating is usually resolved by bending the grating to match the geometry of the X-ray wavefront, thereby improving transmission.

Imaging quality was assessed by placing specimens 9.5 cm from G1 in the direction of G0 (i.e., upstream). Two different specimens were examined, both of which fit in the area of uniform visibility for the measurement system (**Fig. 17a**, orange rectangle). For each sample, the stepping scan was performed<sup>6</sup>, allowing reconstruction of separate images based on absorption, differential phase and dark-field contrast. Magnification associated with the system configuration at Talbot Order 9 was approximately 2, resulting in an effective pixel size on the detector of 38  $\mu$ m (i.e.,

one-half the actual pixel size of 75  $\mu$ m). The first sample consists of polystyrene spheres of 700  $\mu$ m diameter surrounded by air and placed in a capillary. The absorption, differential phase and dark-field contrast images are shown in **Fig. 18a-c**. The polystyrene spheres are clearly visible in all three. The second sample, images shown **Fig. 18d-f**, is a stem of Poaceae surrounded by air in a capillary. Although the absorption and differential phase contrast images capture only the central tap root, the dark field contrast clearly reveals the boundaries of interfaces, including the fine, feather-like secondary roots. The generally good performance is consistent with the quality of the Au fill in the gratings and the measured visibility of the system.

In imaging applications, angular sensitivity, which corresponds to the minimal refraction angle  $(\alpha_{\min})$  that can be detected by the interferometer, is also an important performance metric of the grating interferometer. At the Talbot order 9 used for the setup above, an angular sensitivity of 134 nrad was calculated, using the formula in Ref. 13 and the standard deviation of the signal in the specimen-free region of the differential phase contrast image; significantly, it has been demonstrated<sup>13</sup> that an angular sensitivity of less than 100 nrad is desirable to achieve good contrast. Because angular sensitivity improves with longer distance, the G0 to G2 distance was increased to 73.6 cm, which matched the Talbot order 23. At the same time, contrast in the first specimen was decreased by placing the polystyrene balls in ethanol to reduce both the absorption and refractive index contrast. This low contrast sample was placed 9 cm upstream of G1; magnification associated with this system configuration was approximately 1.6. The imaging results in Fig. 19 (a-c) clearly highlight the power of differential phase contrast imaging where absorption contrast is minimal: the improved angular sensitivity of 90 nrad allowed the structure to be clearly delineated. Furthermore, while the 2D gratings of AR 23 are theoretically suitable for X-ray energies up to the 20 keV used here, the 2 um pitch linear gratings of AR 60 are suitable for energies up to 35 keV.<sup>36</sup> The high contrast phase and dark-field images of the Poaceae roots and polystyrene balls in low contrast environments convey the potential for clinical application of the bottom-up Au filling technology, including in early detection of pulmonary diseases (e.g., emphysema<sup>40</sup>) and breast cancer that require large gratings with deep and high aspect ratio features.

# CONCLUSIONS

Near neutral electrolytes containing different concentrations of Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> with accelerating 50  $\mu$ mol·L<sup>-1</sup> Bi<sup>3+</sup> additive have been used to obtain void-free, bottom-up filling of high aspect features. These include the first demonstration of bottom-up Au filling of via arrays patterned in Si for use as 2D chessboard gratings for X-ray interferometry as well as the highest aspect ratio 2  $\mu$ m pitch trench gratings filled to date. Analysis of current and deposition charge transients obtained under conditions that restrict deposition to the regions of interest enabled understanding and monitoring of the different stages of the filling evolution.

The performance of wafer scale 2  $\mu$ m pitch 1D gratings was tested in a Talbot-Lau X-ray interferometry setup at 20 keV energy. The well-defined peak around a visibility value of 21 % and angular sensitivity in the range of 100 nrad confirm the uniformity and good quality of Au filling in the gratings. The imaging results demonstrate the substantial potential for application of small pitch gratings in the construction of compact ultra-sensitive X-ray interferometers for materials science and biomedical applications as well as the utility of the bottom-up Au filling process for their manufacture.

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### FIGURES



**Figure 1:** a) Schematic of the two-dimensional "chessboard" via array geometry into which Au is electrodeposited. The in-plane pitch is 2w in this schematic of the idealized grating and the via widths are half the pitch. The angular misalignments  $\psi$  and  $\phi$  of the cross-section from coplanarity with the row of vias are indicated. A small nonzero value of the tilt angle  $\psi$  simplifies sectioning because a single cross-section exhibits a repeating pattern of vias in adjacent rows sectioned systematically through their thickness. A nonzero value of the tilt angle  $\phi$ , on the other hand, means that a via sectioned along the midline at its top is not sectioned along the midline at its bottom. This results in the tops and bottoms of the vias being centered in different vias along the section. b) From the top: cleaved edge and overlying field of a via array

grating of 2  $\mu$ m pitch after Au filling; higher magnification view capturing the oscillations in via width from the Bosch etching process. Au filled vias standing nearly clear of the Si, with tapered ends at internal fractures from ductile tearing. With trench width essentially equal to half the pitch, rounding of the via edges allows connectivity of the Si support structure.



**Figure 2:** Cyclic voltammograms for  $0.32 \text{ mol}\cdot\text{L}^{-1}$  Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> + 0.64 mol $\cdot\text{L}^{-1}$  Na<sub>2</sub>SO<sub>3</sub> electrolyte of pH 9.7 containing the indicated Bi<sup>3+</sup> concentrations and specified RDE rotation rates. a) The impact of Bi<sup>3+</sup> concentration at RDE rotation rate of 1600 rpm ( $3200\pi \text{ rad}\cdot\text{min}^{-1}$ ). b-h) The impact of rotation rate at the indicated Bi<sup>3+</sup> concentrations. In all cases, the applied potential was cycled from -0.6 V at 2 mV·s<sup>-1</sup>, deposition was at room temperature, and potentials are relative to SSE. Data was acquired using software compensation for 85 % of the measured 4  $\Omega$  cell resistance (i.e., < 1  $\Omega$  of uncompensated cell resistance). Current density is obtained from measured currents using the nominal area of the 1 cm diameter RDE.



**Figure 3:** Cyclic voltammograms plotted for electrolytes including a)  $0.08 \text{ mol}\cdot\text{L}^{-1} \text{ Na}_3\text{Au}(\text{SO}_3)_2$ , b)  $0.16 \text{ mol}\cdot\text{L}^{-1} \text{ Na}_3\text{Au}(\text{SO}_3)_2$  and c)  $0.32 \text{ mol}\cdot\text{L}^{-1} \text{ Na}_3\text{Au}(\text{SO}_3)_2$  of pH 9.7, all containing 50 µmol $\cdot\text{L}^{-1}$ <sup>1</sup> Bi<sup>3+</sup> at the indicated values of RDE rotation rate, as well as for RDE rotation rates of d) 100 rpm, e) 400 rpm and f) 1600 rpm at the indicated concentrations of Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub>. All the electrolytes

also include 0.64 mol·L<sup>-1</sup> Na<sub>2</sub>SO<sub>3</sub>, and the applied potential was cycled from -0.6 V at 2 mV·s<sup>-1</sup>. Deposition was at room temperature, and potentials are relative to SSE. Data was acquired using software compensation for 85 % of the measured 4  $\Omega$  cell resistance (i.e., < 1  $\Omega$  of uncompensated cell resistance). Current density is obtained from measured currents using the nominal area of the 1 cm diameter RDE.



**Figure 4:** a) Chronoamperometric transients at the indicated potentials for the two specified RDE rotation rates. The considerable impact of potential on the incubation period of slow, passive deposition that precedes activation of the surface is evident. b) Data limited to earlier times to capture differences in the more rapid transients obtained at more negative potentials. Data was acquired without compensation for the measured 4  $\Omega$  cell resistance given the low currents. Current density is obtained from measured currents using the nominal area of the 1 cm diameter RDE. All in 0.32 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> + 0.64 mol·L<sup>-1</sup> Na<sub>2</sub>SO<sub>3</sub> electrolyte of pH 9.7 containing 50  $\mu$ mol·L<sup>-1</sup> Bi<sup>3+</sup>.



**Figure 5:** Scanning electron microscope images of Au electrodeposits in cross-sectioned via array gratings having 23  $\mu$ m deep 2.0  $\mu$ m pitch vias after Au deposition at the indicated potentials. The upper portion of each via is seen at higher magnification below each image (that for -0.74 V being at twice the magnification of the others). The central voids below bridging deposits are widened as an artifact of the ion polishing. Deposition times increase at more positive potentials: 1.3 h, 2.5 h, 3.5 h, 4.5 h, 8 h and 17 h. All in 0.32 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> + 0.64 mol·L<sup>-1</sup> Na<sub>2</sub>SO<sub>3</sub> electrolyte of pH 9.0 containing 50  $\mu$ mol·L<sup>-1</sup> Bi<sup>3+</sup> and rotating at 600 rpm.



**Figure 6:** Scanning electron microscope images of Au electrodeposits in cross-sectioned via array gratings having 23  $\mu$ m deep 2.0  $\mu$ m pitch vias after Au deposition at the indicated potentials. Higher magnification views of specimens from **Fig. 5**. Deposition times and potentials as indicated. The images at -0.78 V highlight (above) the shallow angle of the v-notch formed above the impinged deposits on the sidewalls and (beneath) the start of bottom-up filling. Both images at -0.76 V highlight the region below the void where bottom-up growth is manifest in the microstructure due to electron channeling of the backscattered and/or secondary electrons. The image at -0.74 V captures grain boundaries created during bottom-up filling on the left as well as suggestion of grain growth or recrystallization farther down on the right. All in 0.32 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> + 0.64 mol·L<sup>-1</sup> Na<sub>2</sub>SO<sub>3</sub> electrolyte of pH 9.0 containing 50  $\mu$ mol·L<sup>-1</sup> Bi<sup>3+</sup> and rotating at 600 rpm.



**Figure 7:** Transients of a) current density and b) cumulative deposition charge per projected area for Au electrodeposition on via array gratings having 23  $\mu$ m deep 2.0  $\mu$ m pitch vias at the indicated potentials, including the specimens imaged in **Figs. 5** and **6**. Measured current and charge are converted using the approximately 3 mm × 7.5 mm patterned areas of the substrates. The deposition charge for Au filling of via arrays patterned at 50:50 (square vias and field meeting at a point) and of the stated depth is expected to be 10.9 C·cm<sup>-2</sup> for a 100 % efficient single electron deposition process and the density of gold. Sources of experimental deviation from this value include voids, irregular via dimensions and deposition on the field and within the slot in which the substrate is attached to the rotator spindle. All in 0.32 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> + 0.64 mol·L<sup>-1</sup> Na<sub>2</sub>SO<sub>3</sub> electrolyte of pH 9.0 containing 50  $\mu$ mol·L<sup>-1</sup> Bi<sup>3+</sup> and rotating at 600 rpm.



**Figure 8:** Scanning electron microscope images of Au electrodeposits in cross-sectioned via array gratings having 23  $\mu$ m deep 2.0  $\mu$ m pitch vias after Au deposition at the indicated potentials. The upper region of each is also imaged at two-fold and four-fold higher magnifications beneath. The central bottom-up filled regions are evident in the higher magnification images. Deposition times increase at more positive potential: 2.5 h, 5 h, 6.7 h and 13.3 h. The specimen filled at -0.74 V was shown in a cleaved state in **Fig. 1**. All rotating at 200 rpm about the vertical axis with the specimen suspended in 0.16 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> + 0.64 mol·L<sup>-1</sup> Na<sub>2</sub>SO<sub>3</sub> electrolyte of pH 9.0 containing 50  $\mu$ mol·L<sup>-1</sup> Bi<sup>3+</sup>.



**Figure 9:** Scanning electron microscope images of Au electrodeposits in cross-sectioned via array gratings having 23  $\mu$ m deep 2.0  $\mu$ m pitch vias after Au deposition for the indicated times at the indicated potentials. The three specimens filled at -0.78 V show deposition after truncated bottomup filling followed by upward filling from the impinged sidewall deposits. They capture leveling of fill across the specimen where bottom-up filling halts as well as subsequent conformal filling from passive deposition. The two specimens filled at -0.74 V show the bottom-up filling evolution, also manifesting variation of deposit height albeit from the via bottoms, and uniform fill height upon passivation. All rotating at 200 rpm about the vertical axis with the specimen suspended in 0.16 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> + 0.64 mol·L<sup>-1</sup> Na<sub>2</sub>SO<sub>3</sub> electrolyte of pH 9.0 containing 50  $\mu$ mol·L<sup>-1</sup> Bi<sup>3+</sup>.



**Figure 10:** Transients of a) current density and b) cumulative deposition charge per projected area associated with Au electrodeposition on gratings patterned with via array gratings having 23  $\mu$ m deep 2  $\mu$ m pitch vias at the indicated potentials, including the specimens imaged in **Figs. 8** and **9**. Measured current and charge are converted using the approximately 3 mm × 7.5 mm patterned areas of the substrates, which were rotating at 200 rpm about the vertical axis while suspended in the electrolyte. c) Current density during deposition at -0.74 V on substrates of substantially larger patterned areas rotated in the horizontal orientation at 300 rpm with the spindle immersed in the electrolyte capture the decline of current associated with conformal via filling after approximately 3.5 h. The favorable reproducibility of the deposition process between

the three different specimens is evident. The deposition charge for Au filling of via arrays patterned at 50:50 (square vias and field meeting at a point) and of the stated depth is  $10.9 \text{ C} \cdot \text{cm}^{-2}$  for a 100 % efficient process. Sources of experimental deviation from this value include deposit voiding, irregular via dimensions and deposition on the field and rear surface of the substrate. All in 0.16 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> + 0.64 mol·L<sup>-1</sup> Na<sub>2</sub>SO<sub>3</sub> electrolyte of pH 9.0 containing 50 µmol·L<sup>-1</sup> Bi<sup>3+</sup>.



**Figure 11:** Scanning electron microscope images of Au electrodeposits in cross-sectioned gratings having 66  $\mu$ m deep 1.3  $\mu$ m wide (2.0  $\mu$ m pitch) trenches after Au deposition; widening near the trench openings is reflected in the higher magnification images shown beneath. Filling for the indicated times at the indicated potentials with the specimens suspended into the electrolyte and rotated at 200 rpm about the vertical axis. The deposition at -0.74 V continues approximately 4 h

beyond passivation. All in 0.16 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> + 0.64 mol·L<sup>-1</sup> Na<sub>2</sub>SO<sub>3</sub> electrolyte of pH 9.0 containing 50  $\mu$ mol·L<sup>-1</sup> Bi<sup>3+</sup>.



**Figure 12:** Scanning electron microscope images of Au electrodeposit in cross-sectioned grating having 66  $\mu$ m deep 1.3  $\mu$ m wide (2.0  $\mu$ m pitch) trenches after Au deposition; widening near the trench tops and narrowing toward the trench bottoms are reflected in the higher magnification images. Filling for the stated time and potential, with the specimen suspended into the electrolyte and rotated at 200 rpm about the vertical axis in 0.16 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> + 0.64 mol·L<sup>-1</sup> Na<sub>2</sub>SO<sub>3</sub> electrolyte of pH 9.0 containing 50  $\mu$ mol·L<sup>-1</sup> Bi<sup>3+</sup>. Continued deposition would have yielded truncated bottom-up filling with narrow voids in the lower portion of each trench, as in **Fig. 11** at the same potential.



**Figure 13:** Transients of a) current density and b) cumulative deposition charge per projected area associated with Au electrodeposition on gratings having 66  $\mu$ m deep nominally 1.3  $\mu$ m wide trenches of 2.0  $\mu$ m pitch at the indicated potentials, including the specimens imaged in **Figs. 11** and **12.** c) Current density and d) cumulative deposition charge per projected area obtained during deposition at -0.74 V on substrates having the Pt seed with no additional Au overlayer along with the respective transients for deposition at the same potential on substrates having the conformal Au seed layer from a) and b). Measured current and charge are converted using the patterned area of each substrate. The deposition charge for Au filling of arrays patterned with trenches of the stated width, pitch and depth is 40.6 C·cm<sup>-2</sup> for a 100 % efficient process. Sources of experimental deviation from this value include deposit voiding, irregular trench dimensions and deposition on the field. All rotating at 200 rpm about the vertical axis with the specimen

suspended in 0.16 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> + 0.64 mol·L<sup>-1</sup> Na<sub>2</sub>SO<sub>3</sub> in electrolyte of pH 9.0 containing 50  $\mu$ mol·L<sup>-1</sup> Bi<sup>3+</sup>.



**Figure 14:** Scanning electron microscope images of Au electrodeposits in cross-sectioned gratings having trenches that are  $\approx 60 \ \mu\text{m}$  deep and effectively 0.9  $\mu\text{m}$  wide (AR > 65) at 2.0  $\mu\text{m}$  pitch; visible narrowing approximately one-third of the way down each trench defines the effective trench width for void-free filling. Deposition for the indicated times at the indicated potentials. Higher magnification images to the right capture the trench openings, narrowest regions and trench bottoms. The two highest magnification images of Au fill at the bottom right of the figure show

the impact of local trench width on the width of the central region of bottom-up filling at -0.74 V. All rotating at 200 rpm about the vertical axis with the specimens suspended in 0.16 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> + 0.64 mol·L<sup>-1</sup> Na<sub>2</sub>SO<sub>3</sub> electrolyte of pH 9.0 containing 50  $\mu$ mol·L<sup>-1</sup> Bi<sup>3+</sup>.



**Figure 15:** Transients of a) current density and b) cumulative deposition charge per projected area associated with Au electrodeposition on gratings with 60  $\mu$ m deep nominally 0.9  $\mu$ m wide trenches of 2.0  $\mu$ m pitch at the indicated potentials, including the specimens imaged in **Fig. 14**. Measured current and charge are converted using the patterned areas of the substrates. The deposition charge for Au filling of arrays patterned with trench width equal to half the pitch and of the stated depth is 25.5 C·cm<sup>-2</sup> for a 100 % efficient process. Sources of experimental deviation from this value include deposit voiding, irregular trench dimensions and deposition on the field. All rotating at 200 rpm about the vertical axis with the specimen suspended in 0.16 mol·L<sup>-1</sup> Na<sub>3</sub>Au(SO<sub>3</sub>)<sub>2</sub> + 0.64 mol·L<sup>-1</sup> Na<sub>2</sub>SO<sub>3</sub> electrolyte of pH 9.0 containing 50  $\mu$ mol·L<sup>-1</sup> Bi<sup>3+</sup>.





Figure 16: A schematic of the symmetric X-ray grating interferometry setup, used for quality assessment of the 1D gratings as well as imaging. Source to G0 distance was 20 cm, and the detector was placed immediately behind G2. For the case of the Talbot order 9, which was used for visibility measurements, the length l was 29 cm. For the case of the Talbot order 23, the length was 73.6 cm.



**Figure 17:** a) The visibility map indicates a uniform visibility distribution in the central region (orange rectangle), b) with a pronounced peak at 21 % visibility in the corresponding histogram of values for the individual pixels within this area. The visibility drops rapidly toward the left and right edges of the map due to increasing misalignment of the high aspect ratio (60) Au filled trenches in the *planar* grating and the *divergent* X-ray beam generated by the laboratory X-ray source.



**Figure 18:** a,d) Absorption, b,e) differential phase and c,f) dark field contrast images of two samples: (top) polystyrene balls of 700  $\mu$ m diameter and (bottom) stem of Poaceae in air. The three images of the high contrast polystyrene specimen all capture the fine details in the system. The fine secondary roots on the plant (Poaceae) are only barely evident on the central tap root in the absorption and phase contrast images, but everything is clear in the dark-field image. Scale bars in all images correspond to 1 mm, the magnification factor of 2 for the sample position and system geometry taken into account.





**Figure 19:** a) Absorption, b) differential phase and c) dark field contrast images of the polystyrene balls of 700  $\mu$ m diameter in ethanol. There is negligible contrast in the absorption image and only modest contrast in the dark field image of this low contrast specimen, but the structure is clear in the differential phase image. Scale bars in all images correspond to 1 mm, the magnification factor of 1.6 for the sample position and system geometry taken into account.

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