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Pushing the Limits of Bottom-Up Gold Filling for X-Ray Grating Interferometry

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ABSTRACT

The application of superconformal Bi-catalyzed Au electrodeposition for void-free filling of recessed trenches in X-ray gratings used in phase contrast imaging is detailed. Filling of trenches with aspect ratio (height divided by its width) up to 55 is demonstrated. Uniform bottom-up filling of patterned trench arrays across 100 mm (4 inch) diameter Si wafer is accomplished using a well-defined hydrodynamic flow field across the wafer surface. The filling process and microstructure are examined by scanning electron microscopy of cross-sectioned specimens. The importance of process optimization, from the design of potential (current) programming to electrolyte pH and concentrations of $\text{Na}_3\text{Au}(\text{SO}_3)_2$ and Bi^{3+} , for the filling of high aspect ratio trenches is demonstrated. X-ray phase contrast imaging is used to assay the quality and uniformity of the as-formed gratings as well as demonstrate their application to imaging biological tissue. Successful

void-free Au filling of micrometer range pitch, high aspect ratio trenches in Si gratings promises to advance X-ray grating interferometry and its application to X-ray phase contrast imaging.

INTRODUCTION

Imaging based on X-ray grating interferometry is a promising, fast growing and competitive technique for medical, material science and security applications.^{1,2,3,4} Traditional transmission X-ray absorption measurements scale with atomic number to the 4th power, which permits them to effectively image dense materials such as bone (including Ca, P, etc.) but not soft tissues (composed of C, O, N, H). Differential phase measurement using grating-based interferometry, as in X-ray phase contrast imaging, permits imaging of the low atomic number soft biological tissues with increased contrast and resolution. However, medical diagnostics applications require hard X-rays (> 30 keV) for penetration of the human body, for which the periodic features on these gratings must be: very high aspect ratio (AR, trench height/width, ≥ 50), composed of highly absorbing material such as gold, micrometer, or even sub-micrometer, scale pitch for heightened sensitivity (i.e., contrast), and large area for increased field of view.

Laboratory based phase contrast imaging techniques^{5,6} combine an X-ray source, absorbing and phase shifting X-ray gratings, and an X-ray detector to extract the phase information used for specimen imaging. The X-ray grating interferometer typically employs a set of three gratings located between the X-ray source and the X-ray detector.⁷ The three gratings are commonly referred as the G0 source grating (located near the X-ray source), the G1 phase grating (located near the sample under investigation) and the G2 analyzer grating (located in front of the X-ray detector). The G1 phase grating does not require thick and high aspect ratio Au filled features as it only introduces a phase modulation in the wavefront of the X-ray beam. The G0 and G2 gratings,

on the other hand, must selectively absorb, in periodically defined regions, the entire X-ray intensity coming from the source and the entire X-ray intensity entering the detector, respectively. Data for the absorption, phase shift and dark-field images of a sample are collected simultaneously.¹ Absent the sample, a measurements system using the combined G0, G1 and G2 gratings returns the original source function (in analogy to the sequential application of two Fourier transforms). With the sample in place, the imaging system yields the X-ray phase image of the sample.

High Z metal elements such as gold, platinum, iridium or tungsten that provide strong X-ray absorption are required for the absorbing gratings. Even with such materials, fabrication of gratings with sufficiently high aspect ratio, suitable quality and homogeneity over large areas is challenging, especially etching of the patterned trench array and the subsequent void-free metal filling required to obtain the desired contrast. The difficulty in scaling up these processes is reflected in recent studies of mammography⁸ and chest imaging,⁹ which resorted to stitching together of multiple, smaller gratings in order to increase the field of view, despite all the complications of positioning and alignment. Perhaps the most conceptually simple approach, embossing a patterned substrate with molten metal, as has been demonstrated with lower melting alloys having lower electron densities¹⁰, is not feasible given the higher melting points of gold and the platinum group metals. Instead, microfabrication techniques including LIGA^{11,12} and gold electroplating through insulating silicon templates¹³ have been employed for production of such structures. LIGA processing^{11,12}, also an example of through mask electroplating¹⁴, has been used to produce gratings with very thick gold structures ($> 200 \mu\text{m}$) on gold-coated substrates. However, current LIGA processes are limited to trench arrays patterned with a pitch coarser than $4 \mu\text{m}$. They also require resist exposure on high intensity beam lines at synchrotron light sources, which is both

costly and an impediment for scaling to arbitrarily large substrate sizes. In contrast, silicon-based microfabrication produces both robust and very high aspect ratio templates with lateral dimensions below 1 μm , and the scale-up of substrate size is comparatively straightforward given that commercial manufacturing tools, including for deep reactive ion etching, are commercially available for 300 mm wafers used by the microelectronics industry. Patterned silicon templates have been filled using a silicon oxidation and selective etching to create a through mask geometry for seedless electrodeposition¹⁵ to produce gratings whose trenches have a 1.3 μm pitch and AR = 24. Alternatively, bottom-seeded analogs have been developed using polymer liftoff¹³ or sacrificial metal processes to remove seed layer metal from the field while leaving it at trench bottoms¹⁴. They have also been used for highly conformal deposition of Au¹³ and Ir¹⁶ on trench sidewalls for partial filling that has the effect of halving the patterned pitch. Gold has also been electroplated in silicon templates created using metal assisted chemical etching; the metal catalyst used for the etching remains at the bottom of the trenches and is also used as the seed for the electroplated Au¹⁷. That said, the production of X-ray gratings using both approaches is currently limited by irregular metal growth inside the silicon trenches.

Recent developments in additive derived superconformal electrodeposition processes suggest a path forward. Specifically, a bottom-up gold filling process has been developed wherein Au electrodeposition initiates at the bottom trench surface, propagates upward and automatically terminates to provide void-free filling without overplating onto the grating surface. A schematic of the bottom-up filling process at fixed applied potential is shown in **Figure 1**. In short, deposition is initially slow and uniform on all surfaces, passivated by complexing of sulfite to the gold surface. Absent the Bi³⁺ additive this state would continue throughout the deposition process. However, Bi³⁺ addition and appropriate transport and applied potential(s) lead to filling behavior that is

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3 remarkably different: following a limited “incubation period” of conformal deposition, deposition
4 on the bottom surface activates and continuing growth on the upward moving growth front yields
5 void-free filling, the surface re-passivating when the deposit reaches some distance from the
6 feature opening.
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12 The mechanism of the bottom-up gold filling in these Bi^{3+} containing electrolytes has not been
13 detailed to date although correlations between processing parameters and filling behavior have
14 been established in four previous publications.¹⁸⁻²¹ Both the incubation period of passive
15 deposition that precedes bottom-up filling and the distance at which bottom-up growth terminates
16 due to re-passivation are defined by the applied potential. Not necessarily restricted to a fixed value,
17 the potential is a process design element in combination with electrolyte concentrations and pH.
18 Key to the process is sustained passivation of the feature sidewalls and the field above during the
19 minutes, hours and even days of the bottom-up growth process in tall features. Passivation of the
20 field is substantially impacted by the flow of electrolyte across the surface, especially at more
21 negative potentials where increased flow greatly extends the duration of passivation. Passivation
22 of the sidewalls requires the use of more positive deposition potential for filling of deeper, and
23 possibly higher aspect ratio, features. The electrolyte uses $\text{Na}_3\text{Au}(\text{SO}_3)_2$ as the Au source with
24 Na_2SO_3 added as a supporting electrolyte and micromolar additions of the accelerator bismuth
25 (Bi^{3+}). Void-free, bottom-up filling has already been demonstrated in a variety of trench arrays
26 (trench widths nominally equal to one-half the pitch): 3 μm deep 4 μm pitch (height/width aspect
27 ratio (AR) ≈ 1.5)¹⁸, 5.5 μm deep 1.3 μm pitch (AR ≈ 8.5), 45 μm deep 8 μm pitch (AR ≈ 11)^{19,20}
28 and 210 μm deep 14 μm pitch (AR ≈ 30)²¹. Deposition in 17 μm deep 1.3 μm pitch (AR ≈ 26)
29 trenches, despite being shallower and lower aspect ratio than the last noted, did not exhibit a
30 bottom-up propagation of a planar growth front; rather, nearly void-free filling was obtained
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through partial bottom-up filling coupled with a v-shaped growth front manifesting a gradient of deposition rate down the sidewalls.¹⁹ Deposition on the sidewalls during the incubation period of conformal growth can be problematic in that it increases the aspect ratio of the trench remaining to be bottom-up filled. Sidewall deposits several hundred nanometers thick substantially alter the geometry of the 0.65 μm wide trenches in the 17 μm deep 1.3 μm pitch arrays but are irrelevant for filling of the 4 μm wide trenches in the 45 μm deep 8 μm pitch arrays.

The present study examines the gold filling process in trench arrays of depth and pitch intermediate to those previously examined but with aspect ratios that are substantially higher. In addition, the use of electrolytes that have higher $\text{Na}_3\text{Au}(\text{SO}_3)_2$ and Bi^{3+} ion concentrations is examined. Processing parameters for high aspect ratio features are explored on patterned substrates less than 1 cm^2 in size, which is the size of the specimens in the previous studies. Here, however, the results are subsequently applied to deposition on larger substrates, including fully patterned silicon wafers of 100 mm diameter, for use in X-ray imaging. As in the previous studies, the Bi^{3+} mediated gold filling is conducted on substrates rotating at a rate selected to provide adequate transport of gold ions to the trench array, as reflected in uniform filling across the substrates, and, no less importantly, suppressed deposition on the field above. The difference in fluid flow between analytical studies performed using a rotating disk electrode (RDE) versus the shear field associated with the rotating helicopter blade geometry used for exploratory feature filling experiments with wafer fragments needs to be reconciled for effective translation of the deposition parameters for full wafer plating. To help close the gap between analytical studies and feature filling, a plating geometry is implemented where full wafers are mounted and handled as a RDE.

GOLD FILLING

Experimental Details

Gold filling is examined in silicon gratings consisting of parallel trenches having either 3 μm or 5.25 μm pitch, the trench widths being nominally one-half the pitch, i.e., 1.5 μm and 2.63 μm , respectively, albeit with clear variation along the height of the trenches. The gratings were fabricated on 100 mm silicon wafers, N-type doped with resistivity (0.001 to 0.01) $\Omega\cdot\text{cm}$, coated with a 100 nm thick sputter deposited Cr layer covered by spin-coated MICROPOSIT S1805 positive photo resist. UV-lithography was performed using a SUSS-MA6 mask aligner to expose the coated wafer through a mask having the desired pattern. Developing to remove exposed regions of photoresist was followed by etching of the uncovered areas of the Cr layer using a Cl_2/O_2 plasma. Removal of the remaining photoresist using acetone left the patterned Cr hard mask. Deep reactive ion etching of Si through the Cr mask using the Bosch technique in an Oxford PlasmaLab100 etcher at RF power of 50 W, inductively couple power of 800 W and a substrate temperature of 0 $^\circ\text{C}$ (273 K) was used to create the trenches for gold filling. The chamber pressure was controlled to deliver vertical trench sidewalls: 20 mTorr (2.7 Pa) was used for 3 μm pitch gratings and 25 mTorr was used for 5.25 μm pitch gratings. Details of the etching process are reported elsewhere.²² The etched silicon structures contain cross-bars that bridge the trenches to stabilize the structure against sidewall displacement during subsequent processing. The cross-bars, visible in **Figure 2b**, are spaced periodically, every 50 μm for the 3 μm pitch specimens and every 100 μm for the 5.25 μm pitch specimens, and their locations are staggered by half a period between adjacent trenches. Several wafers were cleaved into fragments, generally 5 mm $\times$ 15 mm, for studies of trench filling. Larger size specimens were used as indicated.

Filling was examined in gratings with four different trench arrays: 45 μm deep 3 μm pitch (AR = 30), 60 μm deep 3 μm pitch (AR = 40), 85 μm deep 3 μm pitch (AR $\approx$ 56) and 100 μm deep

5.25 μm pitch (AR = 38). All but the 45 μm deep 3 μm pitch (AR = 30) trenches have a conformal Pt/ Al_2O_3 layer (20 nm to 30 nm thick platinum on 55 nm thick Al_2O_3) deposited by atomic layer deposition (ALD) over the entire patterned front surface of the gratings that ensures continuous conductivity over the complete trench surface. All the gratings, with and without the Pt/ Al_2O_3 layer, have a Au layer deposited line-of-sight by electron beam evaporation from a metal source. The flux of evaporated Au was at near-normal incidence to the wafers, yielding approximately 70 nm thick Au on the field and trench bottoms but minimal, discontinuous coverage on the (Si or Pt/ Al_2O_3 coated) sidewalls. This Au layer provides (improves) electrical conduction across the specimen and minimizes the nucleation barrier for deposition on the bottom surface. All the 3 μm pitch gratings also have a 100 nm thick Au layer sputter deposited on the rear (unpatterned) surface of the silicon substrate and annealed in air at 493 K for 10 min to create a diffuse contact. Electrical contact for the Au deposition was made exclusively to the front surface on all specimens, and the rear surfaces were shielded from the electrolyte to avoid deposition. For the 45 μm deep 3 μm pitch (AR = 30) trenches, the minimal Au deposition on the sidewalls and absence of Pt requires that conduction from the contact on the field was complemented by conduction through the low resistivity, doped silicon wafer and rear surface Au layer until passive gold deposition on the sidewalls became significant and continuous. Significantly, bottom-up filling is obtained with all variants of the initial seed metallization, and uniformity across all specimens indicates insignificant impact from resistive potential drop.

Deposition on smaller specimens and larger specimens differed not only in the rotation geometry, as detailed earlier, but also in the volume of electrolyte in which deposition was conducted: smaller specimens ($< 1 \text{ cm}^2$, generally $0.5 \text{ cm} \times 1.5 \text{ cm}$) used 40 mL, 120 mL or 400 mL of electrolyte, larger substrates (length or width $> 2 \text{ cm}$) used either 120 mL or 400 mL of

electrolyte, and the full 100 mm wafers used only 400 mL. The electrolytes included 80 mmol/L or 160 mmol/L $\text{Na}_3\text{Au}(\text{SO}_3)_2$ (derived from Technic Gold 25-F replenisher concentrate, which contains 320 mmol/L $\text{Na}_3\text{Au}(\text{SO}_3)_2$, diluted in $18 \text{ M}\Omega\cdot\text{cm}$ water) to which 0.64 mol/L Na_2SO_3 was added. The pH of the as-mixed electrolytes was in the range 9.4 to 9.5. Dilute Bi^{3+} was introduced by anodic dissolution of 99.999 mass % Bi metal; the possibility of parasitic oxidative processes makes the stated concentrations upper bounds. Deposition on wafer fragments was conducted with the specimens rotating about one end from a Pt spindle (i.e., helicopter blade) in the electrolyte. Significant deposition within the slot in the spindle in which the substrates were clamped precludes quantitative evaluation of deposition charge. Deposition on the full wafers was accomplished using a rotating disk geometry where each wafer was mounted using four Pt clamps evenly spaced along its perimeter. The shallow contour of the Pt clamps was designed to minimize interference with the outward spiraling fluid flow across the wafer induced by its rotation. The limited exposed area of the clamps, less than 1 % the planar projected area of the wafer, resulted in minimal contribution to the measured deposition current. The holder is shown with a dismounted wafer after deposition, a mounted wafer prior to deposition, a higher magnification plan-view image of a Au filled grating and the wafer and holder assembled and connected to the rotator undergoing deposition in 400 mL of electrolyte in the 16 cm diameter 8 cm tall cell in **Figure 2**. The plan-view image shows part of a 100 mm wafer after gold filling. The field between trenches and cross-bars spanning them appears brighter than the surface of the gold deposit below the field. A Pt anode, in the form of a wire in the smaller cell and a sheet in the larger cells, was used for all depositions. Attempts to use a Au anode in the Bi-containing electrolyte resulted in a loss of acceleration during overnight deposition that was accompanied by discoloration of the Au anode and precipitation of a salt in the electrolyte.

For experiments with smaller wafer fragments additional $\text{Na}_3\text{Au}(\text{SO}_3)_2$ replenisher was added to the electrolyte between specimens as required to compensate for gold consumption based on coulombs passed assuming 100 % efficiency. Deposition was accompanied by acidification of the electrolyte pH, to as low as 8.5, due primarily to the oxidation of sulfite to sulfate at the Pt anode. Accordingly, the electrolyte pH was checked periodically between specimens and adjusted when it was found to be below 8.5 by addition of NaOH to shift the pH back to between 9.2 to 9.6. Filling of 100 μm deep trenches with width one-half the pitch on a full 100 mm wafer requires 0.04 cm^3 of metallic Au, consuming approximately 0.04 moles of gold sulfite in the electrolyte. As there are only 0.056 moles of gold sulfite in 400 mL of 160 mmol/L $\text{Na}_3\text{Au}(\text{SO}_3)_2$ such a deposition would substantially change the metal concentration in the electrolyte absent adjustment *during* the deposition. Accordingly, the $\text{Na}_3\text{Au}(\text{SO}_3)_2$ replenisher was also added during Au depositions on full wafers and larger wafer fragments. Because of the extended filling times and highly variable deposition rates, these additions were made at irregular intervals and at varying levels of gold ion depletion, although never allowing the $\text{Na}_3\text{Au}(\text{SO}_3)_2$ concentration to deviate more than 8 % from the stated value. No attempt was made to compensate for associated dilution of the nominal Bi^{3+} concentration. The deposition charge of ≈ 1120 C associated with filling of a wafer having 45 μm deep trenches was accompanied by a pH decrease from 9.5 to approximately 8.5. It is possible that drift of electrolyte concentrations and pH, particularly during extended deposition on large substrates, caused some variation in incubation period, filling time or even voided versus void-free filling. Potentials used to control the deposition were taken relative to a Hg/Hg₂SO₄/saturated K₂SO₄ reference electrode (SSE), and no attempt was made to compensate for resistive potential drop within the electrolyte or workpiece contacts.

Procedures for cross-sectioning specimens for optical and scanning electron microscope (SEM) imaging and electron backscatter diffraction (EBSD) mapping are detailed in earlier publications.¹⁸⁻²¹

Processing Parameter Determination

Electroanalytical measurements with defined hydrodynamics are used to explore system behaviors. Such measurements, in combination with relatively limited feature filling experiments, facilitate identification of conditions where highly localized bottom-up feature filling occurs in the Bi^{3+} containing Au electrolyte. This includes experimental determination of parameters for which deposition on the free surface remains suppressed despite ample supply of reactants. A significant finding is that higher rotation rates sustain suppression to more negative potentials and/or higher Bi^{3+} concentration.^{18,20} Indeed, the absence of significant gradients across the hydrodynamic boundary layer adjoining the free surface appears to be central to the onset of sustained localized filling of the most recessed surface segments.

The acceleration of Au deposition induced by Bi^{3+} additives is revealed by cyclic voltammetry and chronoamperometry detailed in earlier studies.¹⁸⁻²¹ At potentials negative of -0.65 V Au deposition rates increase as Bi^{3+} begins to accumulate on the surface. The adsorption process is autocatalytic; positive feedback is particularly evident in rapid increase of current density even on the return scans in cyclic voltammetry in which the overpotential driving deposition is decreasing. Current densities substantially exceed those achieved in the absence of Bi^{3+} additive, increasing until the Au deposition rate is limited by transport of the $\text{Au}(\text{SO}_2)^{3-}$. Higher Bi^{3+} concentrations lead to a more rapid increase in the Au deposition rate while higher $\text{Na}_3\text{Au}(\text{SO}_3)_2$ concentration enables higher deposition rates.²¹

Significantly, in contrast to the large potential range over which acceleration is observed in voltammetry, the spatially localized acceleration of deposition associated with bottom-up feature filling is obtained only at more modest overpotentials for which more complicated Bi^{3+} activation of Au deposition is evident in chronoamperometric experiments. Under these more modest potentiostatic conditions the deposition rate exhibits a markedly non-monotonic dependence on transport conditions. Furthermore, even active deposition is preceded by an extended period of passive deposition before currents rise to higher (magnitude) values reflecting the active state of deposition, as indicated schematically in **Figure 1**; such behavior is observed in chronoamperometry on RDE as well as the bottom-up filling of patterned substrates.¹⁸⁻²¹ This incubation period of passive deposition ranges, remarkably, from seconds to days, its duration increasing strongly at more positive potential and with lower electrolyte pH.

Trench Filling Experiments

Current transients obtained during deposition at different applied potentials on gratings patterned with 60 μm deep 3 μm pitch ($\text{AR} = 40$) trenches are shown in **Figure 3**. The surface of a planar RDE rotated at the same rate and held at the same potential would not activate during this period. The transients at all three potentials exhibit similar features. Focusing on the deposition at -0.78 V, these include: a rising current from the start of deposition that plateaus at ≈ 5 h, followed after 8 h by a further increase of current that ultimately reaches a maximum before descending toward a value consistent with the initial (unaccelerated) rate. The rising current at the start of deposition, from 0 h to 5 h, captures gradual Au coverage of the ALD Pt coated trench sidewalls; the rise reflects the difference between the extremely slow nucleation and growth of Au on the ALD Pt and the slightly less slow deposition rate on the newly formed, but still passivated, Au

surface. The distinction between these processes was not seen in previous studies, the difference being amplified by the large fraction of initially Au-free surface area (i.e., the sidewalls) in the densely packed, high aspect ratio trenches that comprise these gratings. The duration of the incubation period of passive deposition, manifest in the plateau extending to approximately 14 h for filling of the 60 μm deep trenches at -0.77 V, decreases when more negative potentials are used. Both potentiodynamic and galvanodynamic deposition processes have been used to shorten this incubation period while still obtaining void-free bottom-up filling in lower aspect ratio trenches.²⁰ The rising current after the incubation period has been correlated, for smaller trenches, with the start of bottom-up filling. The decreasing current after the period of elevated deposition rate has also been observed during filling of lower aspect ratio trenches and reflects self-passivation of deposition that occurs at a distance from the trench openings related to potential, hydrodynamics and pH. The charge associated with the full deposition process (i.e., the area under the curve) reflects but does not equal Au deposition in the trenches; deposition on the field is a small correction but deposition within the slot of the specimen holder is unquantified. Qualitatively, the charge for the -0.79 V process in **Figure 3** is visibly less than that for the -0.78 V process. The more limited charge associated with the transient period of substantially elevated current density that follows the incubation period and precedes self-passivation, excluding the charge associated with continuing passive deposition on the shrinking sidewall area*, reflects the volume of the trench that is filled by bottom-up deposition. This bottom-up filling charge is clearly smaller at both -0.77 V and -0.79 V than at -0.78 V. Reduced bottom-up filling could be caused by voiding or conformal deposition within the trench volume. The former indicates a failure to fill. The latter,

* The baseline for the passive charge may be estimated to decrease linearly from the plateau value reflecting passive deposition over the entire surface to the final re-passivation value for linear decrease of sidewall area for bottom-up filling at a constant rate.

which can be substantial for filling of narrow features and processes with prolonged incubation periods, complicates filling but is not a failure in and of itself.

The 60 μm deep trenches filled during the current transient are also shown, after cross-sectioning, in **Figure 3**. Truncated bottom-up filling with void-formation is in fact seen at -0.79 V, while void-free filling is observed at -0.78 V and -0.77 V. Thus, as observed previously with lower aspect ratio trenches¹⁸⁻²¹, truncated bottom-up filling at more negative potentials becomes void-free bottom-up filling at more positive potentials. The deposit profiles near the openings are shown at higher magnification as well. The passivation in the chronoamperometry indicates that the final deposition geometries are determined by self-termination, not time limited. These shapes are thus “final” growth shapes, changing toward the end of the deposition processes only through slow, conformal deposition on the uniformly passivated surfaces. The broad horizontal growth front capturing bottom-up (albeit voided) filling at -0.79 V becomes narrower at -0.78 V and disappears into a v-notch at -0.77 V. This geometrical transition captures the impact of cumulative conformal deposition during the incubation period, explaining the decreased charge associated with bottom-up filling at -0.77 V. It is problematic: while a shift to more positive potentials may be necessary to avoid truncated bottom-up filling of deeper trenches, if carried too far the resulting increase of incubation period evident in the current transients can lead to conformal deposits thick enough to preclude bottom-up (and thus truly void-free) filling. That said, conformal growth can yield nominally void-free filling, e.g., with a central seam, if the deposit is v-shaped, as it is at -0.77 V in **Figure 3**. With additional filling through such geometrical leveling implied by the thick deposit on the field due to the extended (35 h) deposition time, the filling profiles at all three potentials are consistent with a passivated growth front that is farther down the trench at more positive potentials. This trend has been observed previously with lower aspect ratio trenches.

The recessed passivation is not intrinsically detrimental to filling as the potential may be progressively advanced to extend filling to higher in the trench.²⁰ Void-free filling to a higher point in the 60 μm deep trenches using a potentiodynamic program that steps progressively to -0.8 V toward the end of the process, is demonstrated in **Figure 4**. The potential history and current density shown in the same figure indicate that filling occurs mainly at -0.77 V and -0.78 V. The initial potential of -0.78 V yields an incubation period of approximately 8 h, consistent with the incubation at -0.78 V in **Figure 3**. Filling at -0.77 V (from 11 h) passivates by 26 h, approximately 5 h earlier than in **Figure 3**, due to the shorter incubation period at -0.78 V. The steps to progressively more negative potentials beginning at 20 h yield incremental deposition charges as filling advances with the potential-dependent location of passivation. The result is a filling process that, in comparison to the depositions at fixed potential in **Figure 3**, is void-free, as with depositions at -0.78 V and -0.77 V, but of intermediate duration and terminating closer to the field, as with deposition at -0.79 V. The complexity suggested by the process is belied by the void-free filling obtained at -0.77 V and -0.78 V alone. In fact, the time at each potential, as well as the potential values and increments, can be varied significantly as long as the majority of deposition occurs in the -0.78 V to -0.77 V range. Shortening the initial activation step will increase the incubation period toward the 18 h obtained in **Figure 3** for -0.77 V, lengthening the filling process and thickening the sidewall and field deposits. Omitting the most negative potential(s) at the end of deposition will halt filling farther from the field. Application of the most negative potentials at the start will, however, yield voided filling, as in **Figure 3** at -0.79 V.

Deposition in 85 μm deep 3 μm pitch ($\text{AR} \approx 56$) trenches at constant potentials is shown with the associated current transients in **Figure 5**. The potential of -0.77 V that gave bottom-up filling in the 60 μm deep trenches yields truncated bottom-up filling in these deeper trenches; voids above

bottom-up filled regions indicate activation of the bottom surface at ≈ 10 h (as per the chronoamperometry) was followed by sidewall activation shortly thereafter. Voiding is also observed at the more positive potential of -0.76 V, the seam-like voids manifesting thick deposits on the sidewalls in the upper half of the trenches. The conformal deposition is consistent with the duration of the incubation plateau, the longest (at the most positive potential) of the experiments in **Figure 3** and **Figure 5**, with only a very slight transient increase of deposition current at ≈ 27 h prior to passivation.

Experimental results such as those in **Figure 3** clearly capture a *negative* bound for potentials compatible with bottom-up filling; voids are observed at potentials negative of this value due to sidewall activation. The value of this negative bound is found to be progressively more positive for deeper trenches.¹⁹⁻²¹ The transition to v-notch filling at -0.77 V in the same figure is no less an indicator the *positive* limit on potential compatible with bottom-up filling. This becomes clear when one considers that sidewall deposition filling half the trench width is incompatible with bottom-up filling and that this sidewall deposit will thicken as the incubation period increases at more positive potentials¹⁹⁻²¹. It is evident that the passive deposit must be thinner, and thus this limiting potential must be more negative to ensure shorter incubation period, for filling of narrower trenches. One thereby reaches the conundrum that for sufficiently tall or narrow (i.e., high aspect ratio) trenches the upper bound for bottom-up filling potentials defined by passive deposition will be negative of the lower bound defined by voiding. In this case there is no potential window for bottom-up filling. The results in **Fig. 3** and **Fig. 5** show that the window that exists for bottom-up filling of $60\text{ }\mu\text{m}$ deep $3\text{ }\mu\text{m}$ pitch ($\text{AR} = 40$) trenches in this electrolyte does not exist for filling of $85\text{ }\mu\text{m}$ deep $3\text{ }\mu\text{m}$ pitch ($\text{AR} = 56$) trenches. The deposition process must be shortened if these deeper, higher aspect ratio trenches are to be filled void-free.

Higher Concentration Electrolyte For Improved Fill

Adsorption studies have clearly shown that the incubation period is lengthened at more positive potentials because the bismuth adsorption required for bottom-up filling is slower¹⁹⁻²¹. Use of a higher Bi^{3+} concentration in the electrolyte should therefore shorten the incubation time. Similarly, active bottom-up filling of Au is expected to be a first order reaction in terms of the $\text{Au}(\text{SO}_3)_2^{3-}$ concentration and thus should be accelerated as its concentration is increased. Deposition in 85 μm deep trenches at fixed potentials using electrolyte in which the Bi^{3+} concentration is increased by a factor of four to 40 $\mu\text{mol/L}$ and the $\text{Na}_3\text{Au}(\text{SO}_3)_2$ concentration doubled to 160 mmol/L is shown in **Figure 6** with the associated deposition transients. The effect of using higher $\text{Na}_3\text{Au}(\text{SO}_3)_2$ concentration has been previously examined for bottom-up Au deposition¹⁶ although the impact of such high Bi^{3+} concentration has not. Truncated bottom-up filling with broad voids having minimal sidewall deposition is evident at -0.77 V and -0.75 V.[†] While bottom-up, void-free filling was obtained in 60 μm deep 3 μm pitch trenches at potentials modulated negative of -0.77 V in the lower $\text{Na}_3\text{Au}(\text{SO}_3)_2$ and Bi^{3+} concentration electrolyte (**Figure 4**), bottom-up filling in the 85 μm deep 3 μm pitch trenches in the higher concentration electrolyte is obtained only the most positive potential of -0.73 V. Equally significant, the width of the passivated horizontal growth surface, with deposition on the sidewalls totaling only a small fraction of the trench width, suggests bottom-up filling of even deeper trenches is possible. Going further will require experimentation with deeper features in combination with a more detailed mechanistic

[†] Alternating trench depth visible in the image shown for -0.75 V is due to variation of etch depth near the cross-bars. Alternating void-size at both -0.77 V and -0.75 V captures variation in filling apparently arising from the impact of the cross-bars on local transport.

understanding of the activation of the bottom-up filling that underlies the incubation period as well as passive deposition rates on the trench sidewalls.

The pH of the electrolyte is also known to accelerate the rates of Bi^{3+} adsorption and Au deposition on planar substrates, shortening the incubation period that precedes bottom-up filling of patterned features.²¹ The impact of pH is seen in the present work through comparison of electrodeposition from pH 9 versus pH 9.5 electrolyte in conjunction with the presence (or absence) of an initial step to more negative potential, prior to filling at more positive potential, to shorten the incubation period.²⁰ The incubation period seen in **Figure 7** for deposition in the 85 μm deep trenches at pH 9, the filled trenches shown in the same figure, is nearly 18 h at -0.73 V even with the first 4 h at -0.75 V. This is significantly longer than the ≈ 14 h incubation period for filling of trenches of the same depth at -0.73 V in electrolyte of pH 9.5 seen in **Figure 6** without the pre-step. The higher pH shortened the incubation period more than the potential pre-step. Comparison of the images in **Figure 6** and **Figure 7** shows that the fill height is essentially unchanged, consistent with use of the same final potentials. However, the sidewall deposit is somewhat thicker in the latter due to the longer period of passive deposition associated with the longer incubation period.

The use of higher electrolyte concentration and potential modulation alone to shorten the incubation period for accelerated bottom-up filling is demonstrated for 60 μm deep 3 μm pitch trenches in **Figure 7**. Filling of these trenches in more dilute electrolyte detailed in **Figure 4** required more than 25 h even with potentials at and negative of -0.77 V. The increased electrolyte concentrations allow the two-step process of 1 h 40 min at -0.75 V followed by 5 h at -0.73 V (potential and current transients also shown in **Figure 7**) to achieve only slightly less filling by just 6 h 40 min, the position being limited by the potential. Passivation is modestly farther from

the field (several micrometers) than with the 85 μm deep 3 μm pitch trenches for which filling ended at the same -0.73 V potential (**Figure 6** and **Figure 7**). However, the sidewall deposits in the 60 μm deep trenches in **Figure 7** are substantially thinner because of the shorter period of passive deposition in the shallower trenches.

Filling of 2.63 μm wide 100 μm deep trenches in the 5.25 μm pitch grating using the electrolyte with 160 mmol/L $\text{Na}_3\text{Au}(\text{SO}_3)_2$ and 40 $\mu\text{mol/L}$ Bi^{3+} , shown in **Figure 8**, is analogous to the filling obtained in narrower trenches. Deposition initiated at -0.75 V followed by progressive stepping to more positive potentials yields truncated bottom-up filling, albeit with an alternating void size even at positions farther from the cross-bars that suggests flow impacts filling over a longer range in the wider features. In contrast, potentiostatic deposition in modestly shallower trenches at -0.73 V is generally void-free. Higher magnification images highlight the microstructure in the upper, middle and lower regions of the latter Au filled trenches, see **Figure 9**, which serves as a fossil record of the underlying deposition process. Large, highly twinned grains are seen in the central regions of the middle and upper portions of the trenches associated with bottom-up growth, with clear demarcation of the grains associated with sidewall deposition. The extended grains in the central growth region are congruent with bottom-up growth involving significant stacking fault formation. The location of the interface between the two different regions of growth is consistent with the thickness of the sidewall deposits near the via opening and above the bottom-up filled region.

Previously, EBSD has been used to analyze the microstructures of Au deposits in 45 μm deep (AR = 11) trenches filled from electrolyte including 80 $\mu\text{mol/L}$ $\text{Na}_3\text{Au}(\text{SO}_3)_2$ and containing 4 $\mu\text{mol/L}$ Bi^{3+} using both potentiodynamic and chronoamperodynamic processes.²⁰ EBSD has also been applied to assess the microstructures of 210 μm deep (AR = 30) trenches that were Au filled

from electrolytes containing both 80 $\mu\text{mol/L}$ and 160 $\mu\text{mol/L}$ $\text{Na}_3\text{Au}(\text{SO}_3)_2$ with a number of Bi^{3+} concentrations using potentiostatic as well as potentiodynamic processes.²¹ EBSD maps of the Au microstructure showed that grains could span the trench width and exceed tens of micrometers in length (discounting twins). However, the grain size in the filled features exhibited substantial spatial variations, both laterally and vertically, within the trenches. Grains that were substantially taller than the trench widths were observed. A much finer grained structure was also observed, often in the same trench. The grain structure was surprisingly disperse considering the bottom-up motion of the growth front during its formation. The mixture was suggestive of partial recrystallization, much like the spontaneous recrystallization that is well known to occur with other metals including Cu Damascene electroplating.^{23,24} In contrast, the large highly twinned grains and demarcation between sidewall and bottom-up growth observed here suggest as-deposited microstructures.

Trench Filling Limits

The results presented here substantially extend the aspect ratio, if not the depth, of trenches for which void-free bottom-up Au filling has been demonstrated. The results reinforce a trend reported previously¹⁹⁻²¹, whereby successful bottom filling of taller features (i.e., more constrained transport) requires a shift to less negative potentials (i.e., slower charge transfer kinetics). Void-free bottom-up filling in these higher aspect ratio trenches is obtained at potentials that are generally positive of those noted previously for lower aspect ratio trenches of similar depth. Likewise, for fixed trench dimensions, increase of both the $\text{Au}(\text{SO}_3)_2^{3-}$ and Bi^{3+} concentrations results in faster feature filling and increased width of the bottom-up growth front albeit with a shift to more positive potential for bottom-up filling to prevail.

Trenches with aspect ratio of 30 up to 56 have been successfully filled leading one to ponder possible extension to even higher aspect ratio features. Lacking a quantitative mechanistic model for the additive-derived feature filling, an empirical formulation has been detailed that accounts for the competition between active bottom and passive sidewall deposition rates as well as increase of the feature aspect ratio due to passive deposition during the incubation period that must subsequently be bottom-up filled.¹⁹⁻²¹ Accordingly, the maximum aspect ratio of trenches that can be filled without sidewall-impingement is given by

$$\frac{h}{w} = \frac{v_b}{2v_s} \left(1 - \frac{2t_i v_s}{w} \right) \quad [1]$$

where the sidewall and bottom-up growth rates are v_s and v_b , respectively, the trench width and height are w and h , respectively, and the incubation period prior to the start of bottom-up filling is t_i . Values for the active bottom up growth rate have previously been reported^{19,20} to lie in the range $v_b \approx (6.5 \text{ to } 7.5) \mu\text{m/h}$ with the passive growth rate on the sidewalls of $v_s \approx 0.13 \mu\text{m/h}$ just above the upward moving front and $0.025 \mu\text{m/h}$ near as well as on the field reflecting passive deposition rates at both -0.78 V with $24 \mu\text{mol/L Bi}^{3+}$ as well as -0.8 V with $4 \mu\text{mol/L Bi}^{3+}$ in electrolytes containing $80 \text{ mmol/L Na}_3\text{Au}(\text{SO}_3)_2$.

For comparison, the sidewall deposits just above the growth front at -0.78 V in **Fig. 3**, between $0.50 \mu\text{m}$ and $0.63 \mu\text{m}$ thick (the range due to scalloping of the underlying silicon), accrued during 21.5 h at -0.78 V with $80 \text{ mmol/L Na}_3\text{Au}(\text{SO}_3)_2$ and $10 \mu\text{mol/L Bi}^{3+}$ yields a smaller value for the average sidewall deposit rate v_s in the range $(0.023 \text{ to } 0.029) \mu\text{m/h}$. This result is included in a summary of sidewall growth rates in **Figure 10** that were derived from the thickness of the sidewall deposits divided by the deposition times. The datapoint pairs manifest sidewall scalloping from the etch process and generally uniform deposition observed in multiple trenches. These values exclude data from regions within $5 \mu\text{m}$ of the trench openings where the passive deposition rates

on the sidewalls decrease toward the even slower rates observed on the field (presumably related to the greater hydrodynamic shear that passivates the free surface) yielding thickness gradients visible in the higher magnification images in **Figure 3**. Sidewall growth rates are included for specimens filled both at fixed potential and using potentiodynamic control. Datapoints from the latter are plotted versus the time average of the potential, the value being generally within +2 mV, and no more than +6 mV, from the potential used for the principle bottom-up filling step. Data from two classes of specimens that are considered lower bounds to the sidewall growth rates relevant for void-free filling are also included: specimens exhibiting a v-notch profile due to sidewall impingement and specimens where bottom-up filling has approached within 5 μm of the trench openings. It is obvious that the former values, with growth rates evaluated from half the trench width divided by the deposition time despite growth having terminated upon impingement, are lower bounds to actual growth rates. Values obtained from the latter are considered lower bounds due to the gradient of sidewall thickness near the trench openings. Higher passive deposition rate is clearly obtained with higher $\text{Na}_3\text{Au}(\text{SO}_3)_2$ concentration, the data not inconsistent with the doubling one might expect with a first order dependence on concentration going from 80 mmol/L to 160 mmol/L. The growth rates on the sidewalls of these high aspect ratio trenches in the 80 mmol/L electrolyte are approximately one-third of the values noted previously for -0.78 V to -0.8 V within substantially wider trenches although consistent with the rates noted near and on the field. Absent measurements from a sequence of partially filled specimens the growth rate of the bottom surface can only be inferred from chronoamperometry.

The values of $v_b \approx 7.5 \mu\text{m/h}$ and $v_s \approx 0.13 \mu\text{m/h}$ obtained during filling of lower aspect ratio trenches yield a maximum aspect ratio of trenches that can be bottom-up filled of 29. While the inclusion of a nonzero incubation period lowers this value, it has been previously noted that

the observed gradient of sidewall thickness could enable geometrical leveling²¹. Use of sidewall deposition rate consistent with even the highest values $v_s \approx 0.03 \mu\text{m/h}$ to $v_s \approx 0.04 \mu\text{m/h}$ found in **Figure 10** yields a maximum aspect ratio of approximately 190 to 250 for trenches that can be bottom-up filled. This is unquestionably decreased by the extended incubation period at these more positive potentials; it may also be decreased with v_b at these more positive potentials as well. Nonetheless, bottom-up filling is readily attained in trenches of aspect-ratio 56 in this study, and the filling geometries suggest filling to even higher aspect ratios is possible. It remains to be seen whether values approaching, or even exceeding, 200 can be realized. Work continues in this direction.

X-ray Phase Contrast Imaging by Interferometry with Au Filled Gratings

Experimental Details

The bottom-up electrodeposited Au filled gratings were characterized using a laboratory X-ray grating interferometry setup. The system was composed of a microfocus X-ray source from SIGRAY Inc and EIGER X-ray detector from Dectris Ltd. with a pixel size of $75 \mu\text{m}$. The total length of the setup was 75 cm. The microfocus X-ray source used an electron acceleration voltage of 42 kV and an electron current of 1.5 mA. A design photon energy of 20.0 keV for X-ray grating interferometer was selected using a 9th Talbot order symmetric geometry. For this characterization, only gratings with a pitch of $3 \mu\text{m}$ were used. Gratings with bottom-up Au filled trenches $45 \mu\text{m}$ and $60 \mu\text{m}$ deep were used for G0 and G2, respectively. Bottom-up filled gratings of two different sizes, one with patterned area $2.5 \text{ cm} \times 3.0 \text{ cm}$ and the other $3.5 \text{ cm} \times 3.5 \text{ cm}$, were used for G2. Both the Au filled $45 \mu\text{m}$ and $60 \mu\text{m}$ deep structures are well suited for photon energy of 20.0 keV, delivering very high absorption of X-ray flux through the Au filled trenches and minimal

absorption in the Si walls and overlying silicon substrate. The G1 phase grating was made of silicon only and was fabricated using the same silicon reactive ion etching described previously. It had a pitch of 3 μm with a height of 25 μm that produces a phase shift of π for the photon energy of 20 keV.

Visibility and Imaging

The “visibility” is a figure of merit for the quality of the X-ray interference that can be used to evaluate the performance of an X-ray interferometer.⁶ Systems with higher visibilities yield better X-ray phase images, including higher contrast, of the imaged sample. Among other parameters, the visibility depends strongly on the quality of the X-ray gratings, including the relative absorption in the silicon and Au-filled regions and their uniformity, both in dimension and absorption. Uniformity of the visibility in the field of view of the system is thus also a measure of variations in patterning and filling across the grating. The first X-ray grating interferometer constructed with bottom-up filled gratings used the smaller G2 grating, restricted to an area of 1.8 cm $\times$ 1.8 cm by the holder with sample field of view further reduced to 0.95 cm $\times$ 0.95 cm by the geometric magnification ($M \approx 1.9\times$) of the system. **Figure 11a** shows a visibility map for an area about 18 mm on a side. It exhibits a peak visibility of 0.243 and appears uniform to the eye. Such values are difficult to realize using gratings of small pitches and laboratory microfocus X-ray sources that deliver a polychromatic X-ray spectrum.⁶ The histogram of the visibility values in the map shown in **Figure 11b** confirms the uniformity. **Figure 11c, d, and e** show the absorption, phase and dark-field images of a sample made of polystyrene colloids of 700 μm . They are collected simultaneously. The benefit of using phase contrast imaging is reflected in higher signal to noise in the differential phase contrast image as compared to that in the absorption contrast

image. The dark-field image obtained using the X-ray grating interferometer delivers information of the structure of the sample that cannot be resolved with the resolution provided by this X-ray detector.^{4,25}

Figure 12a displays the visibility map of the X-ray grating interferometer achieved using the larger bottom-up gold filled G2 grating. In this case the full 3.0×3.0 cm area of the grating was used, providing a 1.6×1.6 cm field of view. The visibility peak in the inset histogram is at 0.22 and is uniform aside from the circular region at the center originating from the lithography and the dark region at the corner due to reduced trench depth toward the edges of the silicon wafer. **Figure 12b** shows the differential phase contrast image of mouse kidneys embedded in solid paraffin using the system characterized in **Figure 12a**.

The X-ray interferometer with the bottom-up Au filled X-ray gratings characterized in **Figure 12a** was also used to acquire phase tomography scans of a mouse heart. A total of 721 projections were obtained while rotating the sample from 0° to 180° around an axis normal to the beam direction over a total acquisition time of approximately 60 h. The data was reconstructed using the ASTRA tomographic toolbox assuming²⁶ a “fanflat” beam geometry. Several slices of the three-dimensional reconstruction are shown in **Figure 13**. The numbered lines in the first tomographic slice denote the positions and orientations of the similarly numbered slices shown for the orthogonal directions of the tomographic volume. The images were taken with an effective pixel size of $38 \mu\text{m}$. Such laboratory phase contrast imaging opens the possibility of heart studies in much greater detail.²⁷ The high contrast observed in the soft tissue is the ultimate proof of the performance of the X-ray grating interferometer that can be achieved when using bottom-up gold filled gratings. These results highlight the promise of using this approach for void-free, bottom-up gold deposition in suitably patterned Si wafers to fabricating high contrast grating. Further X-ray

characterization and imaging demonstrations with the bottom-up gold filled X-ray gratings will be described in more detail elsewhere.

CONCLUSIONS

Near neutral pH 9.5 electrolytes containing 80 mmol/L $\text{Na}_3\text{Au}(\text{SO}_3)_2$ with 10 $\mu\text{mol/L}$ Bi^{3+} and 160 mmol/L $\text{Na}_3\text{Au}(\text{SO}_3)_2$ with 40 $\mu\text{mol/L}$ Bi^{3+} have been used to obtain void-free, bottom-up filling of high aspect ratio trench arrays in Si for use as diffraction gratings. The combination of the higher $\text{Na}_3\text{Au}(\text{SO}_3)_2$ and Bi^{3+} concentrations enabled void-free bottom-up filling of trenches with aspect ratio of 56. This is nearly twice the highest aspect ratio, 30, of trenches that have been previously bottom-up filled, and those were much easier to fill being wider trenches. The increase in aspect ratio that accompanies conformal deposition during the incubation period makes filling the 1.5 μm wide trenches much more challenging. The combination of higher Bi^{3+} and $\text{Na}_3\text{Au}(\text{SO}_3)_2$ concentrations used here provides a route for filling of even higher aspect ratio trenches, a result of Au deposition rates on the active versus passive surfaces that differ by more than two orders of magnitude. Examination of the gratings for X-ray imaging shows very good values and uniformity of visibility. The resulting system performance enables promising X-ray phase contrast imaging, and tomographic reconstruction of a mouse heart demonstrates the quality of the produced gratings. The ability to fill increased aspect ratio trenches achieved here will allow more effective X-ray interferometry at the higher energies required for clinical diagnostics.

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FIGURES

Figure 1: Gold deposition in fully metallized trenches that exhibits the bottom-up evolution that can be obtained in $\text{Na}_3\text{Au}(\text{SO}_3)_2$ based electrolytes containing micromolar concentrations of Bi^{3+} .

Key features are: a) an initial incubation period of uniformly slow passive deposition on all surfaces, b-c) the inception and continuation of active deposition localized to the bottom-up surface and d-e) re-passivation of deposition at a controllable distance from the field of the substrate and self-termination of the deposition process. The width of the onset in b) and re-passivation in d) include variations across the substrate. The active deposition in c) may also continue to accelerate, rather than plateau as pictured, through the onset of re-passivation. The process is pictured here for constant applied potential (potentiostatic) but can be obtained also with potentiodynamic as well as galvanodynamic control.

Figure 2: a) The lower, wafer mounting, surface of the wafer holder used for full wafer depositions is seen in the rear. The shallow, off-center heads of four Pt bolts that can be rotated for mechanical mounting and electrical contact of the wafer are visible. The bolts traverse the thickness of the Teflon body and are connected using platinum washers and nuts to Pt wires that run radially to the rotator shaft. A 100 mm diameter wafer patterned with a grating, dismounted

after bottom-up gold filling, is in the foreground. b) A grating with 100 μm deep 5.25 μm pitch trenches is seen in planview at higher magnification after Au deposition; the cross-bars, staggered in adjacent trenches, are spaced by 100 μm . c) A wafer is shown mounted on the holder prior to gold filling. d) The upper side of the wafer holder is connected to the rotator, with its lower surface and attached 100 mm grating immersed in 400 mL of electrolyte during deposition. The radial Pt wires on the holder are not visible at the 300 revolutions per minute (RPM, 600π rad/min) rotation rate. The Pt plate anode rests on the bottom of the cell approximately 1 cm from the wafer (cathode) and is connected to the potentiostat cable by a Pt wire running up the inner, right side of the cell. The reference electrode, seen on the left side of the cell, is inside a potassium sulfate filled cell that is separated from the electrolyte by a Vicor tip. Off-center positioning of the rotating holder within the cell creates a wave in the front of the rotating holder that is visible at higher magnification.

Figure 3: Current transients associated with Au electrodeposition on wafer fragments patterned with 3 μm pitch, 1.5 μm wide, nominally 60 μm deep trenches. Deposition times increase moving to more positive potentials: 17 h at -0.79 V, 21.4 h at -0.78 V and 35 h at -0.77 V. Scanning electron microscope images of the corresponding Au electrodeposits in the cross-sectioned gratings are shown beneath. Depth variation captures variable etching across the

source wafer. Higher magnification views of the filling profiles are included. All in 80 mmol/L $\text{Na}_3\text{Au}(\text{SO}_3)_2$ + 0.64 mol/L Na_2SO_3 electrolyte containing 10 $\mu\text{mol/L}$ Bi^{3+} at a rotation rate of 300 rpm.

Figure 4: Scanning electron microscope images of Au electrodeposit in cross-sectioned grating on a wafer fragment 2.5 cm $\times$ 3 cm in area patterned with 3 μm pitch, 1.5 μm wide, nominally 60 μm deep trenches after gold deposition. It was filled using a potentiodynamic process: 11 h at -0.78 V, 9 h at -0.77 V, 5.25 h at -0.775 V, 1 h at -0.78 V, 1 h at -0.79 V then 2 h at -0.8 V. The current transients and potential histories associated with filling of the specimen are shown beneath; data at the start of deposition reflect open circuit potential. In 80 mmol/L $\text{Na}_3\text{Au}(\text{SO}_3)_2$ + 0.64 mol/L Na_2SO_3 electrolyte containing 10 $\mu\text{mol/L}$ Bi^{3+} at a rotation rate of 300 rpm. The noise in

the current density noise is presumably related to convection and the oscillating cell geometry associated with the large substrate (working electrode) rotating around the central spindle.

Figure 5: Scanning electron microscope images of Au electrodeposits in cross-sectioned gratings on wafer fragments patterned with 3 μm pitch approximately 1.5 μm wide and 85 μm deep trenches after gold filling at -0.77 V for 22.3 h and -0.76 V for 45.4 h. Higher magnification view of the specimen filled at -0.76 V captures narrow voids as well as microstructure reflected sidewall deposits and central bottom-up growth. The current transients associated with the trench filling are shown to the left. All in 80 mmol/L Na₃Au(SO₃)₂ + 0.64 mol/L Na₂SO₃ electrolyte containing 10 μmol/L Bi³⁺ at a rotation rate of 300 rpm.

Figure 6: Scanning electron microscope images of Au electrodeposits in cross-sectioned gratings on wafer fragments having 3 μm pitch, 1.5 μm wide, approximately 85 μm deep trenches after Au deposition for 3 h 10 min at -0.77 V, 17 h at -0.75 V and 21 h 15 min at -0.73 V. Higher magnification images of the upper and lower regions are inset in the last. The current transients associated with the trench filling are shown beneath. All in 160 mmol/L $\text{Na}_3\text{Au}(\text{SO}_3)_2$ + 0.64 mol/L Na_2SO_3 electrolyte containing 40 μmol/L Bi^{3+} at a rotation rate of 300 rpm.

Figure 7: Scanning electron microscope images of Au electrodeposits of cross-sectioned gratings having 3 μm pitch, 1.5 μm wide trenches after two-step Au deposition in approximately 85 μm deep trenches for 4 h at -0.75 V followed by 27 h at -0.73 V in electrolyte with initial pH 8.96 and in nominally 60 μm deep trenches for 1 h 40 min at -0.75 V followed by 5 h at -0.73 V in electrolyte

with initial pH 9.46. Higher magnification images highlight the passivated deposits at the tops of the trenches. The current transients and potential histories associated with the potentiodynamic controlled filling of the two specimens are shown beneath; data at the start of deposition reflect open circuit potential. An incubation time of ≈ 3 h before bottom-up filling begins is seen for filling of the 60 μm deep trenches in higher pH electrolyte. An incubation time of 18 h is seen with the 85 μm deep trenches in the lower pH electrolyte. Both in 160 mmol/L $\text{Na}_3\text{Au}(\text{SO}_3)_2$ + 0.64 mol/L Na_2SO_3 electrolyte containing 40 $\mu\text{mol/L}$ Bi^{3+} at a rotation rate of 300 rpm.

Figure 8: Scanning electron microscope images of Au electrodeposits in cross-sectioned gratings having 5.25 μm pitch, 2.63 μm wide, nominally 100 μm deep trenches after Au deposition. a) Deposition for 17 h at -0.75 V followed by 2 h at -0.76 V, -0.77 V, -0.78 V and then 1 h at -0.79 V in electrolyte with initial pH 9.16 and b) 20 h at -0.73 V in electrolyte with initial pH 9.09. The latter specimen is somewhat shallower. All in 160 mmol/L $\text{Na}_3\text{Au}(\text{SO}_3)_2$ + 0.64 mol/L Na_2SO_3 electrolyte containing 40 $\mu\text{mol/L}$ Bi^{3+} at a rotation rate of 300 rpm.

Figure 9: Scanning electron microscope images at higher magnification of Au electrodeposits in cross-sectioned grating having $5.25\ \mu\text{m}$ pitch, $2.63\ \mu\text{m}$ wide, nominally $100\ \mu\text{m}$ deep trenches after Au deposition for 20 h at $-0.73\ \text{V}$ in electrolyte with initial pH 9.09. All in $160\ \text{mmol/L}$ $\text{Na}_3\text{Au}(\text{SO}_3)_2 + 0.64\ \text{mol/L}$ Na_2SO_3 electrolyte containing $40\ \mu\text{mol/L}$ Bi^{3+} at a rotation rate of 300 rpm.

Figure 10: Experimental deposition rate on trench sidewalls obtained from deposit thickness divided by deposition time is plotted versus deposition potential. Data is shown for growth in 1.5 μm wide trenches in electrolyte with 80 mmol/L $\text{Na}_3\text{Au}(\text{SO}_3)_2$ + 0.64 mol/L Na_2SO_3 containing 10 μmol/L Bi^{3+} and 160 mmol/L $\text{Na}_3\text{Au}(\text{SO}_3)_2$ + 0.64 mol/L Na_2SO_3 containing 40 μmol/L Bi^{3+} as well as in 2.63 μm wide trenches in the latter. All depositions were conducted at a rotation rate of 300 rpm. Data pairs reflect the range of thickness measured in cross-sections. Data from specimens filled using potentiodynamic control are included with the average growth rates plotted at the time-average of the potential. Specimens exhibiting a v-notch profile are included with deposition rates obtained using one half the trench width as lower bounds to the deposition rate. Rates obtained from deposits within 5 μm of the trench opening are also included as lower bounds to the deposition.

Figure 11: a) and b) Visibility map and visibility histogram of an X-ray interferometer using bottom-up gold filled $3.0\ \mu\text{m}$ pitch $1.5\ \mu\text{m}$ wide gratings of $45\ \mu\text{m}$ and $60\ \mu\text{m}$ depth as absorbing G0 and G2 gratings, respectively. An area of $1.8 \times 1.8\ \text{cm}$ of a $2.5\ \text{cm} \times 3.0\ \text{cm}$ G2 grating was used. c), d) and e) Absorption contrast, differential phase contrast and dark-field contrast of a sample consisting of $700\ \mu\text{m}$ diameter polystyrene spheres in a micropipette tip.

Figure 12 a) Visibility map and visibility histogram (inset) of an X-ray interferometer using two bottom-up gold filled 3.0 μm pitch 45 μm and 60 μm deep gratings as absorbing G0 and G2 gratings, respectively. The G2 grating used was 3.0 cm $\times$ 3.0 cm. b) Differential phase contrast image of mouse kidneys embedded in solid paraffin.

Figure 13: Phase tomographic reconstruction of mouse heart using the X-ray grating interferometer with bottom-up Au filled X-ray gratings that was characterized in **Figure 12a**. Several slices through different directions of the three-dimensional reconstructed volume are displayed.

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