with high surface roughness may lead to the formation of voids and/or seams **106** when the rough opposing side walls impinge.

[0061] Deposition in the presence of 50 μmol/L MBIS, shown in row (b) of FIG. **2**, results in smoother overburden **110** above the widest trench, as shown in FIG. **2**, row (b), column (**1**); however, centerline voids and/or seams **106** appear near the top of the smallest trenches shown in column (**4**). Increasing the MBIS concentration to 80 μmol/L, shown in row (c) of FIG. **2**, yields a smoother free surface **110**; however, voids and/or seams **106** are still evident at the top of finest trenches shown in row (c), column (**4**), although they are smaller than for the 50 μmol/L shown in row (b) of FIG. **2**. A further increase in the MBIS concentration to 100 μmol/L, shown in row (d) of FIG. **2**, leads to void-free filling for all features shown. Comparison between the additive-free, 50, 80, and 100 μmol/MBIS concentrations shown in rows (a), (b), (c), and (d) respectively, performed for the same duration and potential, show progressively less overburden **112** above the filled features **102**, which may show the inhibition provided by MBIS. This effect is most notable over the widest features, shown in column (**1**) of FIG. **2**. A further increase of MBIS concentration to 150 μmol/L, shown in row (e) of FIG. **2**, was shown to lead to a sharp decrease in the overall deposition rate. In row (e) of FIG. **2**, very limited deposition occurred on the free surface **104** while substantial filling of the trenches **102** occurred. The smaller trenches **102** shown in columns (**2**)-(**4**) of FIG. **2**, row (e), are completely filled while the growth front in the widest features shown in column (**1**) of FIG. **2**, row (e), has a well-defined v-notch shape **114**. This shows a superconformal film growth mode in column (**1**), row (e), of FIG. **2**; whereby the effect of a linear gradient of the sidewall **116** growth velocity with trench depth is evident and deposition at the bottom **118** of the trench **102** is substantially progressed compared to the neighboring free surface **104**.

[0062] In order to show a more detailed view of shape evolution during feature filling, a series of samples were examined as a function of deposition time at −0.925 V SCE in the 100 μmol/L MBIS electrolytic solution. The results for five different trench widths as shown in FIG. **3** wherein row (a) has a trench width of 590 nm, row (b) has a trench width of 520 nm, row (c) has a trench width of 305 nm, row (d) has a trench width of 160 nm, and row (e) has a trench width of 130 nm. For reference purposes, the Cu-seeded substrate t=0 is shown prior to Ni deposition in the column (**1**) of FIG. **3** for each trench width. The columns, from left to right, show the deposition of Ni after 0 seconds in column (**1**), 25 seconds in column (**2**), 50 seconds in column (**3**), 100 seconds in column (**4**), 150 seconds in column (**5**), 200 seconds in column (**6**), and 300 seconds respectively in column (**7**). The buildup of Cu **202** on the top **204** and bottom **206** surfaces, relative to the sidewalls **208**, reflects the nature and limitations of the physical vapor deposition or sputtering process used to form the seed layer **210**. Examination of the filling images after 25 seconds of deposition show a substantially conformal Ni layer **212** along the entire surface profile, where the height 214 of the bottom surface **206** and the sidewall **208** thickness **216** are almost the same. The extent of Ni deposition in the recessed regions **218** may be compared to the integrated deposition charge derived from the chronoamperometry transient. Because the surface area changes significantly during feature filling, a comparison of nominal thickness value may be only considered for the first 25 seconds and the last 100 seconds from 200 to 300 seconds, assuming that there is minor area change occurring for the respective cases.

[0063] Between 25 seconds and 50 seconds, shown in column (**2**) and column (**3**) respectively, the two finest features, shown in rows (d) and (e), are shown to be filled while almost negligible Ni deposition has occurred on the top surface **204**. The geometry of the feature filling is such that electrode area change effects may be most strongly during the filling of the smallest and highest aspect ratio features. In the three wider trenches shown in rows (a), (b), and (c), a gradient in the deposition rate on the sidewalls **208** has clearly developed as a function of width, similar to that noted earlier in row (e) of FIG. **2** The amount of Ni deposited on the bottom surface **206** is shown to be substantially the same to that on the sidewalls **208** immediately adjacent to the bottom **206**. Notably, the amount of Ni deposited on the sidewalls **208** of the larger features may exceed half of the width of the two narrowest trenches, shown in rows (d) and (e), consistent with those features which may have already been filled by sidewall collision, followed by a geometric zipping process The transient depletion of MBIS within the trench may result in the sloping sidewalls or v-notch shape and may be critical to the overall void-free filling process.

[0064] Between 50 seconds and 100 seconds, as shown in columns (**3**) and (**4**) of FIG. **3**, growth continues on the bottom **206** and sidewalls **208** of the 305 nm wide trench shown in row (c) of FIG. **3**. The slope associated with sidewalls **208** did not change substantially between 50 seconds and 100 seconds, as shown in columns (**3**) and (**4**), row (c), of FIG. **3**. This may show a transition back to a conformal growth mode as reflected by the constant sidewall growth velocity during this time increment. Evolution of the growth front in the widest trench, shown in row (a) of FIG. **3**, may also support this. In the absence of any compositional gradients, continued growth on such a v-notched surface geometry may result in a planar surface by an effect known as geometrical leveling. Indeed, following trench filling, significant growth is shown to begin on the adjacent free surface **204** and the remaining cusp shape in the larger features is filled congruent with geometric leveling.

[0065] FIG. **3** shows that trench filling may be associated with three stages, a brief period of near conformal growth, followed by the development of sloping sidewalls, and the subsequent onset of impingement of opposing sidewalls. The remaining cusp or v-notch shape may then be filled by geometric leveling. A key role of MBIS may be the development of sloping sidewalls, which may be associated with transient depletion of the MBIS flux within the trench. Deposition in the presence of MBIS was shown to be substantially uniform on the pattern density length scale, making the MBIS process a viable manufacturing solution in the context of conventional Damascene processing

[0066] The potential dependence of trench filling is shown in FIG. **4** for a fixed MBIS concentration of 100 μmol/L and a fixed deposition time of 300 seconds. The results for four different trench widths as shown in FIG. **4** wherein column (**1**) has a trench width of 520 nm, column (**2**) has a trench width of 305 nm, column (**3**) has a trench width of 160 nm, and column (**4**) has a trench width of 90 nm. The rows, from top to bottom, show the deposition potential wherein row (a) has an potential of −0.850 V SCE, row (b) has an potential of -0.875 V SCE, row (c) has an potential of −0.900 V SCE, row (d) has an potential of −0.925 V SCE, and row (e) has an potential of −0.950 V SCE.