Effects of Acetic Acid, Tartaric Acid and Pb UPD on Cu Electrodeposition in Sub-Micron Trenches

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The effects of acetic acid, tartaric acid, and Pb-mediated underpotential deposition (UPD) on the filling characteristics of copper electrodeposition in sub-micron trenches were studied. In the absence of other electrolyte additives, potentiostatic and galvanostatic depositions from electrolytes containing organic acids were capable of producing dense filling in sub-micron trenches due to higher deposition rates at the trench bottoms compared to the side-walls and adjacent surfaces surrounding the recessed features. The mechanism for dense filling of trenches from depositions in the organic acid containing electrolytes did not appear to match previously identified mechanisms for superfilling associated with surfactant effects. Instead, the differential deposition rates across the trench profile were attributed to textural and/or structural differences in the copper seed layer as the copper deposition rates were enhanced at both the bottom and adjacent surfaces surrounding the trenches, or sidewalls of the trench depending on the organic acid species present in the electrolyte. The organic acids induced conformal and smooth depositions improving with increasing concentration. Pb-mediated UPD yielded smooth, conformal films relative to non-mediated deposition under otherwise identical conditions. The density of the UPD mediated films was best at higher Pb coverage during Cu deposition.

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Extensive research efforts over the past few decades have led to the development and continued improvement and understanding of electrodeposition processes suitable for deposition of dense films of copper in recessed sub-micron features for integrated circuit applications.1–6 Processes that yield locally enhanced deposition at the bottom of recessed features (termed “bottom-up”, superconformal filling, or “superfilling”) rely on additives that adsorb with differential coverage on the various surfaces of the recessed features causing locally inhibited or enhanced deposition rates of the copper film.7,8 Since the development of the first electrodeposition process for superconformal filling of interconnect features, the Damascene process, models have been developed that successfully predict the characteristics of the systems capable of superfilling.10–12

The most commonly studied superconformal filling systems are acid copper sulfate based electrolytes with small amounts of organic additives that act to produce differential deposition rates. The earliest demonstrated system capable of superconformal filling was an acid copper sulfate based electrolyte containing an organic additive acting as a leveling agent that suppresses the deposition rate at a magnitude proportional to its relative coverage.9 Due to diffusional effects, more leveler reaches the surface of the field and upper regions of the sidewalls of recessed features, leading to suppression of copper deposition at those areas and enhanced deposition rate at the bottom of the recessed features. The leveling agent is consumed and incorporated into the copper film. Films deposited by this method can have relatively large impurity concentrations due to incorporation of the leveler.10,11

A well-characterized system using an acid copper sulfate electrolyte with three or four additives has also been extensively studied and successfully modeled by the Curvature Enhanced Accelerator Coverage (CEAC) model.2,6,10–12 During deposition, superfilling is achieved when a rate-accelerating additive (typically a thiol) competitively displaces a rate-suppressing additive (often a polymer), at advancing concave surfaces. Displacement of the inhibiting additive leads to enhanced deposition rates at concave surfaces, such as the copper films advancing from the bottom of recessed features.

More recently, a third electrodeposition method capable of producing superfilling by negative differential feedback (NDR) has been demonstrated with several metals including Cu deposited from either alkaline or acid based electrolytes.14–17 In these systems an inhibiting additive passivates the surface of substrate. At a sufficient overvoltage, deposition initiates at local defects in the passivating film. On flat substrates these systems yield characteristic patterns with areas of localized deposition distributed within areas of minimal deposition. In model integrated circuit (IC) systems, experimental techniques can cause the disruption of the inhibiting film to preferentially occur at the bottom surfaces of recessed features, leading to superfilling.

The study of organic additives for copper electrodeposition systems, such as those mentioned above, and also for printed circuit board applications is an active area of research.18–23 Replacing traditionally used acid-based electrolytes with weak organic acid based electrolytes has recently been studied for copper deposition in through-holes on printed circuit boards.24,25 These studies showed that replacement of H2SO4 with acetic acid improved film quality. The authors suggested that molecular acetic acid interacts with other organic additives to form a complex that binds to the copper electrode surface, helping to mediate deposition, and to improve film quality.

Another strategy that provides adsorbed species which mediate deposition is under potential mediated deposition (UPD), which has been demonstrated as a method for inducing two dimensional growth of an electroplated metal.26–28 The mediating metal is less noble than the deposited metal and acts as a surfactant within a well-defined range of potentials, forming up to a monolayer on the surface of the growing film. The surfactant monolayer increases the density of two-dimensional nuclei on the surface of the depositing metal while suppressing formation of three-dimensional nuclei on uncompleted monolayers of the depositing film, thereby inducing two-dimensional growth in systems that typically exhibit three-dimensional growth. A previous study on the effects of using UPD mediated deposition (with Pb as the mediating metal) of Cu showed that 0.5–1.4 atomic percent Pb was incorporated into the film depending on deposition conditions and supporting electrolyte.29

In this study, we examine the effects of acetic and tartaric acids on the deposition characteristics of Cu in sub-micron trenches, using the organic acids both as an additive and as a replacement for sulfuric acid. The electrolytes were composed of 0.19 M – 0.30 M copper sulfate or copper acetate with organic and sulfuric acids in various concentrations. In this study we also examine filling characteristics of...
Figure 1. Cyclic voltammetry measurements of (a) 0.19 M CuSO₄ + 0.007 M H₂SO₄ + HOAc at the indicated HOAc concentrations and (b) 0.19 M CuSO₄ + 0.007 M H₂SO₄ + HTar at the indicated HTar concentrations on the Cu foil working electrode between −370 and −1370 mV vs MSE at a scan rate of 10 mV/s.

Figure 2. Cyclic voltammetry measurements from 0.15 M Cu(ClO₄)₂ + PbClO₄ at the indicated concentrations on the Cu foil working electrode between −330 mV and −860 mV vs MSE (for 0 M PbClO₄) and −300 mV and −790 mV vs MSE (for 0.30 M PbClO₄) at a scan rate of 10 mV/s.

the UPD mediated deposition of copper in sub-micron trenches with electrolytes of 0.15 M copper perchlorate and 0.30 M lead perchlorate. Although the studied features are larger than current state of the art, we employ them in this study as a model system for determining filling effects of the various additives.

Experimental

Electrolytes for organic acid studies were composed of 0.19 M – 0.30 M reagent grade copper sulfate or copper acetate, 0.01 M to 0.79 M of either acetic (HOAc), tartaric acid (HTar) or sulfuric acid and > 18Mohm-cm water. Electrolytes for Pb mediated deposition were composed of 0.15 M copper perchlorate hydrate, 0.3 M lead perchlorate hydrate, and > 18Mohm-cm water.

Substrates for deposition were sections of a planar silicon wafer with lithographically patterned trenches of various dimensions in the dielectric layer. In this study, we focus on deposition in the smallest trenches with dimensions of approximately 360 nm deep by 300 nm wide with 200 nm lateral spacing between trenches. Barrier layers of Tantalum and Tantalum Nitride were sputtered onto the patterned dielectric, and a copper seed layer was sputtered onto the barrier layer. The seed layer was measured by SEM cross section to be 59 nm thick at the field between the trenches, 14 nm at the sidewall and 51 nm at the bottom of the trenches. IBM T.J. Watson kindly supplied the patterned substrates used in this study.

Electroplater’s tape was used to mask off approximately 0.5 cm² areas for potentiostatic and galvanostatic depositions. For voltammetry measurements, a 5 mm diameter copper foil with predominantly (111) texture was used as the working electrode. The foil was polished with 1200 grit abrasive and rinsed with ultra-pure water prior to each measurement. During depositions, the substrates were mounted vertically and parallel to a copper foil counter electrode, ∼ 1 cm from the working electrode. A PAR 263A potentiostat was used for all depositions and voltammetry. A saturated mercury/mercury sulfate electrode (MSE) was used as the reference electrode for experiments in copper sulfate based electrolytes while a copper foil pseudo reference was used in experiments from copper acetate based solutions, and all potentials mentioned hereafter are in reference to the MSE electrode unless otherwise noted for Tafel analysis. A Mettler Toledo Seven Excellence pH and conductivity meter was used for pH and conductivity measurements.

Samples were cleaved and mounted in epoxy for cross-sectional analysis. Cross-sectional samples were polished with silicon carbide and diamond suspensions to 1 micron prior to final finishing by ion milling. Film thickness measurements were made via SEM micrographs from the mounted samples.

Results

Deposition on planar electrodes.—Figure 1 shows cyclic voltammetry measurements on a planar copper working electrode for sulfuric based solutions with varying concentrations of acetic and tartaric acids. The voltammetry data show that acetic and tartaric acids inhibit deposition. The conductivity of the solutions decreased by 6% over the concentration ranges shown for the acetic acid containing solutions and increased by 13% over the concentration ranges shown for the tartaric acid containing solutions. The acetic acid voltammetry trends were consistent with those previously observed for copper deposition from acetic acid containing electrolytes.

Figure 2 shows cyclic voltammetry measurements on the copper foil for copper perchlorate and copper perchlorate + lead perchlorate solutions. The Pb UPD peak was evident at approximately −650 mV to −700 mV to the MSE reference electrode. The presence of the Pb UPD layer inhibited deposition and also caused the open circuit potential of copper to shift 30 mV positive relative to the MSE reference (from −330 mV to −300 mV) of that in the Pb free electrolyte.

Deposition on Patterned Surfaces from Organic Acid-Containing Electrolytes.—Figures 3–5 show cross-sectional SEM
micrographs of copper films deposited at various overpotentials from acetic acid, tartaric acid and sulfuric acid based electrolytes. The films deposited from organic acid based electrolytes were substantially smoother and more conformal than the sulfuric acid based electrolytes, which produced rough and non-uniform deposits unsuitable for IC applications. The ability of the organic acids to induce conformal smooth films increased with increasing overpotential. Films deposited from all of these solutions showed indications of enhanced deposition rates at the bottom and fields of the trenches at low overpotentials.

Figures 3 and 4 show that the relative copper deposition rates at the various regions of the trench were affected by overpotential using the organic acid based electrolytes. The apparent flux at the field, walls and bottom of the trenches were measured from a minimum of ten trenches at each deposition potential for the acetic acid and tartaric acid containing electrolytes by converting thickness measurements at each area to an average effective current density. At overpotentials less than 80 mV, the acetic acid based electrolyte did not produce smooth or conformal deposits suitable for an estimate of the local average current density; neither did the sulfuric acid based electrolyte, at any overpotential sampled, due to the roughness and poor uniformity of the films. Figures 6 and 7 shows these apparent fluxes in a Tafel plot as well as the ratios of the fluxes at each section of the profile as a function of overpotential. These data show that in the organic acid containing electrolytes the ratio of deposition flux at the bottom/sidewall was largest at low overpotentials and decreased toward a 1:1 ratio as the overpotential increased into the diffusion limited regime. The largest ratio of current density at the bottom relative to the sidewalls of the trenches was achieved with copper acetate based solutions containing acetic and sulfuric acids.

Figures 8–14 show polished cross-sectional SEM micrographs of copper films deposited in trenches during potentiostatic and galvanostatic depositions in acetic acid and tartaric acid based solutions. The deposition potentials for potentiostatic depositions were chosen to maximize the deposition rate at the bottom of the trenches relative to the sidewalls, as indicated in Figure 7. For the depositions from acetic and tartaric acid containing electrolytes an enhanced deposition rate at the bottom of the trenches was evident, and dense films free of major defects were observed for deposition times sufficient to fill the trenches. The current densities for galvanostatic depositions were chosen to provide dense filling, as shown in Figure 11, or demonstrate conformal deposition occurred at greater current densities as shown in Figures 12 and 13. With sufficient deposition time to fill the trenches, center seams due to conformal deposition were observed in the galvanostatically deposited films at the larger current densities used. A small amount of porosity distributed uniformly across the profiles was observed at the bond line of the seed layer. We believe that this porosity resulted from a residual oxide film on the surface of the seed layer that was reduced during deposition.

Deposition on Patterned Surfaces with Pb UPD Mediation.—

Figure 15 shows polished cross-sectional SEM micrographs of copper films deposited in trenches during potentiostatic depositions from the perchlorate-based solutions. Depositions on patterned substrates were performed at 360 mV overpotential relative to the Cu$^{2+}$/Cu open circuit potential in the Pb containing electrolyte to achieve a nearly complete monolayer of Pb coverage in Pb containing electrolytes. The micrographs show that Pb-mediated deposition resulted in dense conformal Cu films with the expected center seam in the filled trench as a result of the conformal deposition, while non-mediated deposition was rough and not suitable for interconnect applications. The non-mediated deposition showed a preference for growth at the sidewalls of the trenches. Multiple attempts to cycle the deposition potential around the Pb UPD potential during Cu deposition to achieve differential coverage and possible superconformal Cu deposition were unsuccessful. The quality of the deposited copper film was also a function of the relative Pb coverage during deposition. At Pb coverages maintained at less than ~50% of a monolayer, the deposited films exhibited nanoscale porosity (not shown in Figure 15).

Figure 3. Cross-sectional SEM micrographs of copper films deposited on trenched substrates from 0.30 M CuSO$_4$ + 0.79 M HOAc (pH = 2.25) at (a) 80 mV overpotential [−420 mV vs MSE] for 155 sec, (b) 120 mV overpotential for 84 sec and (c) 200 mV overpotential for 54 sec.

Figure 4. Cross-sectional SEM micrographs of copper films deposited on trenched substrates from 0.19 M CuSO$_4$ + 0.016 M HTar (pH = 2.26) at (a) 40 mV overpotential [−390 mV vs MSE] for 229 sec, (b) 80 mV overpotential for 125 sec and (c) 500 mV overpotential for 14 sec.

Figure 5. Cross-sectional SEM micrographs of copper film deposited on trenched substrate from 0.19 M CuSO$_4$ + 0.009 M H$_2$SO$_4$ (pH = 2.26) at 160 mV overpotential [−510 mV vs MSE] for 49 sec.
Figure 6. Tafel plots of Cu current density at the sidewall, field and bottom of the trenched features as measured from cross-sectional SEM micrographs from depositions on patterned substrates from (a) 0.30 M CuSO₄ + 0.79 M HOAc, (b) 0.19 M Cu(OAc)₂ + 0.12 M HOAc + 0.38 M H₂SO₄, (c) 0.19 M Cu(OAc)₂ + 0.12 M HOAc + 0.4 M H₂SO₄ and (d) 0.19 M CuSO₄ + 0.016 M HTar electrolytes. Data is plotted as a function of cathodic overpotential from the Cu²⁺/Cu open circuit potential.

Discussion

We first address if the enhanced deposition rates at the trench bottoms relative to the sidewalls in the acetic or tartaric acid containing electrolytes is consistent with any of the well-established mechanisms of superfilling. The organic acids indeed induced conformal deposition as required by a leveling mechanism. However, the deposition rate at the field was not strongly suppressed relative to the bottom of the trenches as expected for a superfilling film deposited by such a mechanism. There was no rate-increasing additive coupled with an inhibiting additive as required for superfilling by the CEAC mechanism, and the films did not exhibit the characteristic convex overfill bump as expected for films deposited by the CEAC mechanism. Finally, the voltammetry measurements did not show the characteristic ‘S’-shaped hysteresis associated with the NDR mechanism.

Figure 7. Ratios of the bottom/sidewall current densities as a function of overpotential from the indicated electrolytes. Data is plotted as a function of cathodic overpotential from the Cu²⁺/Cu open circuit potential.

Figure 8. Cross-sectional SEM micrographs of copper films deposited on trenched substrates from 0.30 M CuSO₄ + 0.79 M HOAc at −120 mV overpotential [−460 mV vs MSE] for (a) 84 sec and (b) 163 sec.

- 0.19 M Cu(OAc)₂ + 0.12 M HOAc + 0.40 M H₂SO₄
- 0.19 M Cu(OAc)₂ + 0.12 M HOAc + 0.38 M H₂SO₄
- 0.19 M CuSO₄ + 0.016 M HTar
- 0.30 M CuSO₄ + 0.79 M HOAc
One possible mechanism for this may be connected to different deposition kinetics at the sidewall vs. the bottoms and fields. To test this, we performed least squares fitting of the apparent flux curves in Figure 6 to the Butler-Volmer Equation,

\[ j = j_0 \exp \left( \frac{(1 - \alpha)nF\eta}{RT} \right) - \exp \left( \frac{\alpha nF\eta}{RT} \right), \]

as well as the ratios of these fluxes (Figure 7). The constraint of equal equilibrium potentials at each section of the profile was applied during fitting analysis, and analysis was performed for both a single step reduction of copper and a two-step reduction of copper (Cu^{2+} first reduced to Cu^{+}, then reduced to Cu) for the tartaric and acetic acid depositions to find the charge transfer coefficients and exchange current densities. The results were nearly identical for single and two-step reductions. Figure 16 shows an example of the best fit data points.
Figure 14. Cross-sectional SEM micrographs of copper films deposited on trenched substrates from 0.19 M CuSO₄ + 0.016 M HTar at 40 mV overpotential (−390 mV vs MSE) for (a) 229 sec, (b) 455 sec and (c) 1011 sec.

Figure 15. Cross-sectional SEM micrographs of copper film deposited on trenched substrate from 0.15 M Cu(ClO₄)₂ for (a) 34 sec and (b) 34 sec in a trench of width 500 nm and 0.15 M Cu(ClO₄)₂ + 0.30 M PbClO₄ for (c) 9.3 sec and (d) 54 sec. All depositions were performed at −690 mV vs MSE. The arrows indicate characteristic seams due to conformal deposition.

Figure 16. Least squares fitting results (shown by dashed lines) for (a) Tafel data and (b) the ratios of the calculated current density at the bottom, sidewall and trench as a function of overpotential for Cu²⁺/Cu reduction for films deposited from Cu(OAc)₂ + 0.12 M H₂OAc + 0.40 M H₂SO₄. The plotted points indicate mean current densities, and the error bars indicate the range of calculated current densities as determined from individual measurements of film thickness. The largest error in these data, as a percentage of the mean thickness, corresponded to measurements at the sidewall at deposition overpotential of 120 mV. The range of measured film thicknesses for that data point was 3 to 17 nm with an average of 10 nm. The mean measured film thicknesses and their average ranges across all overpotentials were: 41 nm mean with +18 nm/−14 nm range at the sidewall; 166 nm mean with +34 nm/−35 nm range at the trench bottom; and 96 nm mean with +40 nm/−31 nm range at the field.
copper was deposited. In fact, a recent study demonstrated that in sub-micron trenches, the structure of the evaporated seed layer can be different on the walls of the trench compared to the bottom and field.\textsuperscript{31} In the cited study, the seed layer on sidewalls of submicron trenches exhibited non-uniform grain structure consisting of relatively large Cu crystals distributed in a nano-crystalline Cu matrix, while the seed layer at the trench bottoms and surrounding fields consisted of uniform, equiaxed polycrystalline grains. If textural or structural variation as demonstrated in this study was present in the seed layer of the substrates used in the current study, this could have resulted local variations in exchange current density and symmetry coefficients as calculated in Table I. Pairing the suspected effects of the seed layer texture and structure with the effects of the organic acid on film smoothness and conformity could have then yielded the dense films grown with enhanced deposition rates at the bottom and field as shown in Figures 8–14. For films that were deposited galvanostatically, we observed trends that aligned with those observed during potentiostatic depositions. At current densities of 5 mA/cm\(^2\) (Figure 11) corresponding to measured overpotentials in the range of up to 150 mV during deposition, we observed enhanced deposition rates at the fields and bottoms of the trenches. Galvanostatic depositions at current densities of 8 and 20 mA/cm\(^2\) (Figures 12, 13) corresponding to deposition potentials up to approximately 250 mV and 375 mV respectively during deposition yielded conformal depositions as also might be expected from data in Figure 6. We also note that galvanostatically deposited films appeared smoother with increasing current density as might be expected from the potentiostatic deposition results.

In order to further probe the effects of seed layer texture and structure, we studied the effects of Pb-mediated UPD on deposition of Cu on the patterned substrates. Films were deposited with Pb mediation with the intention that the surfactant Pb monolayer would uniformly induce conformal 2D growth across the trench profiles. By inducing 2D growth, we aimed to obscure any possible differences in local deposition kinetics due to seed layer effects. Conformal depositions were evident in the Pb mediated depositions shown in Figure 15. When depositing under the same conditions from the perchlorate-based electrolytes without the Pb mediation, the Cu films preferentially deposited at the sidewalls (even for diffusion limited conditions) in a 3D growth mode with minimal deposition at the bottom and field of the trenches as evident in Figure 15. This deposition pattern was in contrast to the films deposited from copper sulfate or copper acetate based electrolytes which showed preferential deposition at the bottom and field compared to the sidewall of the trenches at activation-controlled potentials. These deposition characteristics also suggested an inherent difference in the local deposition rate due on local texture and/or structure of the surface and interactions with species in the electrolytes. We suggest that pairing an additive that induces smooth and conformal deposition with deposition on a seed layer with inherent textural or structural differences along the profiles of recessed features could be an attractive method for future studies of superfilling.

For the Pb-mediated depositions, the UPD technique was capable of strongly influencing the kinetics of the film growth, and thereby induced conformal growth across the trench profiles. Even though a measurable Pb content was not detected by EDS in the films grown by UPD mediation, we suggest that these films likely contain small quantities of Pb (≈1 at% or less) since previous studies using the same technique showed that some Pb was incorporated into Cu films.\textsuperscript{23} While the use of Pb is undesirable for environmental and health related reasons, other metals that demonstrate UPD behavior on Cu might be suitable for UPD mediated deposition for IC applications. Zn has recently been demonstrated as a mediator for 2D Cu deposition by deposition schemes employing galvanic displacement of UPD deposited Zn with Cu.\textsuperscript{32}

### Conclusions

Filling of sub-micron trenches by copper electrodeposition in acetic acid and tartaric acid containing electrolytes as well as Pb-mediated UPD electrodeposition of Cu films was studied. Enhanced deposition rates were observed at the bottom of the trench profiles relative to the sidewalls in acidic electrolytes containing organic acids. The relative deposition rates at the bottom of the trenches relative to the sidewalls was a function of the overpotential with the greatest bottom/side wall deposition rate ratio occurring at low overpotentials in the organic acid electrolytes. At large overpotentials, conformal films were deposited from organic acid-containing electrolytes. Dense filling of the trenches from organic acid electrolytes was demonstrated at low overpotentials as well as two-step deposition processes to optimize the deposited film. Dense filling of the trenches was also demonstrated by galvanostatic deposition at current densities corresponding to overpotentials that yielded sufficiently enhanced deposition rates at the fields and bottoms of the trenches during potentiostatic depositions. Pb mediated UPD was also capable of inducing conformal deposition across the profile of the trenched substrates.

The film morphologies and voltammetry characteristics for the deposition processes that yielded dense films in the trenches were not consistent with any well-known superfilling models. Tafel analysis suggested deposition kinetics differed along the trench profile, which resulted in the observed differential growth rates. The differences in local deposition rates were attributed to possible variations in the texture/structure of the seed layer across the trench profiles.

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### Table I. Calculated exchange current densities (\(j_0\)) Cathodic Symmetry Coefficients (\(\alpha_c\)) from least squares fitting of data from Figure 6.

| Electrolyte | \(j_0\) Field [mA/cm\(^2\)] | \(j_0\) Sidewall [mA/cm\(^2\)] | \(j_0\) Bottom [mA/cm\(^2\)] | \(\alpha_c\) Field | \(\alpha_c\) Sidewall | \(\alpha_c\) Bottom | \(\alpha_c\) Bottom/Field | \(\alpha_c\) Bottom/Sidewall |
|-------------|-----------------|-----------------|-----------------|-------------|-------------|-------------|-----------------|-----------------|
| 0.30 M CuSO\(_4\) + 0.79 M HOAc | 0.93 | 0.18 | 2.40 | 0.08 | 0.17 | 0.05 | 0.64 | 0.29 |
| 0.19 M Cu(OAc)\(_2\) + 0.12 M HOAc + 0.38 M H\(_2\)SO\(_4\) | 2.48 | 0.06 | 5.66 | 0.05 | 0.20 | 0.04 | 0.77 | 0.20 |
| 0.19 M Cu(OAc)\(_2\) + 0.12 M HOAc + 0.40 M H\(_2\)SO\(_4\) | 1.88 | 0.05 | 4.70 | 0.09 | 0.23 | 0.06 | 0.70 | 0.26 |
| 0.19 M CuSO\(_4\) + 0.016 M H\(_2\)Tar | 0.82 | 0.34 | 1.63 | 0.11 | 0.17 | 0.07 | 0.63 | 0.41 |
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