

# In Situ STM of 3-Mercaptopropanesulfonate Adsorbed on Pt(111) Electrode and Its Effect on the Electrodeposition of Copper

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The adsorption of 3-mercaptopropanesulfonate (MPS) molecule on a Pt(111) single-crystal electrode and its effect on the deposition of Cu have been examined using in situ scanning tunneling microscopy (STM). MPS admolecules were irreversibly adsorbed in a largely disordered adlayer on bare Pt(111) in 0.1 M HClO<sub>4</sub>, irrespective of the presence of chloride, the concentration of MPS, and the applied potential. In comparison, the MPS admolecules readily formed a highly ordered molecular structure identified as  $(4 \times 2 \sqrt{3})$  arct on Pt(111) precoated with a monolayer of Cu adatoms. The MPS admolecules were adsorbed upright on Pt(111). The cyclic voltammetric results show that the MPS adlayer on Pt(111) would inhibit Cu deposition because the addition of 10  $\mu$ M MPS to the electrolyte of 0.1 M HClO<sub>4</sub> + 1 mM KCl + 1 mM Cu(ClO<sub>4</sub>)<sub>2</sub> reduced the amount of the Cu deposit by half, even in the presence of chloride. The texture of the Cu deposit also varied with the surface state of the Pt(111) electrode as the Cu film grew in three-dimensional islands and smooth flakelike morphology on the MPS-modified and Cu-coated Pt(111) electrodes, respectively. In situ STM results indicated that the MPS admolecules stayed afloat rather than buried by the Cu deposit.

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The damascene deposition of Cu has attracted a great deal of attention lately as modern semiconductor processing presses toward a more compact architecture.<sup>1-6</sup> The copper interconnects between chips are largely manufactured by electrodeposition in a plating bath, which usually contains an accelerating agent [3-mercaptopropanesulfonate (MPS) or bis-3-sodiumsulfopropyl disulfide (SPS)], a blocking agent [poly(ethylene glycol)], and chloride.<sup>5-8</sup> These components enable faster Cu deposition at the valley than at the necks and walls of a trench.

The mechanism behind superconfocal deposition of Cu has been extensively discussed.<sup>9-16</sup> It seems that the adsorption of MPS or SPS on the electrode surface with or without chloride is closely relevant to their accelerating effect on Cu deposition. Molecularresolution scanning tunneling microscopy (STM) imaging has been used to examine the adsorption of MPS and SPS at Cu(111) and Cu(100) electrodes, showing a largely disordered adlayer on Cu(111), but MPS forms a  $c(2 \times 2)$  on Cu(100) in the absence of chloride.<sup>17,18</sup> On Au(111), the organization of MPS and SPS varied greatly with the potential, and ordered adlattices were observed only at potentials in excess of 0.7 V [vs reversible hydrogen electrode (RHE)].<sup>19</sup> In addition to the prominent gold-sulfur bond, the sulfonate functional group in the MPS molecule also interacts with the gold electrode, yielding parallel molecular orientations.<sup>19,20</sup> Subsequently, the chemical nature of the electrode could be important to the adsorption of MPS and SPS molecules.

Vapor-deposited thin films of Pt-group metals of Ru, Os, Ir, Pt, etc., have been used as barriers in seedless Cu deposition.<sup>21-23</sup> However, the adsorption of an accelerating agent such as MPS or SPS on Pt-group metals is largely unexplored. Since we have worked with Pt-group metal electrodes for more than 10 years, studying the underpotential of copper, specifically adsorbed anions, and the adsorption of organosulfur compounds on Pt(111) electrodes,<sup>24-28</sup> we then tried to apply our expertise to unravel the adsorption of MPS on Pt(111) and how this molecular adlayer affected the deposition of Cu.

The results obtained here show that MPS molecules were strongly adsorbed on bare and Cu-modified Pt(111) electrodes, but the ordered MPS adlayer was produced only on Cu-modified

Pt(111), identified as  $(4 \times 2 \sqrt{3})$  rect. Also, we observed the different textures of the Cu deposit on the Pt(111) electrode with or without an MPS adlayer.

# Experimental

The Pt(111) electrodes used in the STM and voltammetric experiments were homemade. The pretreatment of the Pt(111) electrode involved annealing first with a hydrogen torch, followed by slow cooling in quartz saturated with ultrapure hydrogen.<sup>24-26</sup> It was then transferred quickly to the STM cell, which was equipped with Pt wires as the counter and reference electrodes. All the potentials reported here are converted into a scale of an RHE. The thermally formed oxide on the Pt(111) electrode needed to be removed before the deposition of the MPS molecules. This was accomplished by ramping the potential from the open-circuit potential (OCP) at  $\sim 0.85$  to 0.05 V, followed by a positive sweep at 50 mV/s. The potential was then held at 0.3 V, and MPS-containing perchloric acid was then added. The STM scanner was a typical A head (Veeco, Santa Barbara) with a maximal scan size of 500 nm. The tip was a tungsten tip etched by ac in 1 M KOH. Nail polish was applied to coat the whole tip for insulating purposes. The potential of the tip electrode was set normally at 0.4 V, and the feedback current was adjusted to 1 nA.

The electrochemical cell used for voltammetry had a threeelectrode configuration including an RHE and a Pt counter electrode. The potentiostat was a CHI 614 (Austin, TX). The potential was mostly swept at 50 mV/s. Suprapure perchloric acid (HClO<sub>4</sub>) and potassium chloride (KCl) were purchased from Merck (Darmstadt, FRG). Triple-distilled water (Lotun Technology Co., Taipei) was used to prepare the electrolytes. Copper perchlorate  $[Cu(ClO_4)_2]$  and MPS were obtained from Aldrich (St. Louis, MO).

# **Results and Discussion**

*Cyclic voltammetry.*— Figure 1 shows the cyclic voltammograms obtained with the Pt(111) electrode immersed in 0.1 M HClO<sub>4</sub> + 1 mM KCl + 1 mM Cu(ClO<sub>4</sub>)<sub>2</sub> with (dotted trace) and without (solid trace) 10  $\mu$ M MPS molecules. For both profiles, the potential scans started at 0.85 V, first going negative at 50 mV/s until 0.05 V, where the scan direction was reversed. Without MPS, the underpotential deposition (UPD) of Cu resulted in two sharp, reversible peaks at 0.56 and 0.73 V before bulk deposition of Cu commenced at 0.25 V.<sup>24,26</sup> The MPS molecules were likely ad-

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**Figure 1.** Cyclic voltammograms recorded at 50 mV/s with Pt(111) electrode in 0.1 M HClO<sub>4</sub> + 1 mM Cu(ClO<sub>4</sub>)<sub>2</sub> + 1 mM KCl without (dotted trace) and with (solid trace) 10  $\mu$ M MPS. The irreversibly adsorbed MPS adlayer caused negative shifts of the potentials for the UPD and OPD processes. The amount of Cu deposited on Pt(111) was reduced in the presence of MPS.

sorbed on Pt(111) at the OCP ( $\sim 0.85$  V), which resulted in marked shifts of the UPD and overpotential deposition (OPD) of Cu by 0.3 and 0.1 V, respectively.

We extrapolated the amount of OPD and UPD layers of Cu from the charges under the stripping peaks at 0.35 V (A) and at 0.55 V (A'). The presence of 10  $\mu$ M MPS reduced the amount of charge under peak A by 50% compared with that observed without MPS. Subsequently, either adsorbed or dissolved MPS molecules inhibited the deposition of Cu on the Pt(111) electrode coated with an MPS adlayer. This is somewhat unexpected because MPS accompanied by chloride should have yielded more, not less, Cu deposition, as suggested by all relevant studies.<sup>4,5,15,18,29</sup> Although it is possible that this inconsistency arose from unlike concentrations of components in the electroplating solution, we contend that the rate of Cu<sup>2+</sup> reduction could vary with the chemical nature and atomic structure of the electrode. For example, MPS molecules could be adsorbed more strongly and packed more tightly on Pt(111) than on Au(111)and Cu(111), which slowed down the reduction of Cu<sup>2+</sup>. The MPS adlayer was stable against potential cycling between 0.05 and 0.85 V, as revealed by steady voltammetric profiles (not shown).

In situ STM imaging of MPS adlayer on Pt(111).— Figure 2 reveals in situ STM images acquired with Pt(111) at 0.3 V in 0.1 M HClO<sub>4</sub> + 10  $\mu$ M MPS. Monatomic steps separating wide terraces [typical surface characteristics of a Pt(111) electrode] are seen in Fig. 2. Step ledges frequently ran parallel to the main axes of the Pt(111) electrode, and the atomic structure at the terrace site was



**Figure 2.** (Color online) [(a)–(c)] Successively finer STM images showing the surface morphology and molecular structures of MPS adlayer deposited on bare Pt(111) in 0.1 M HClO<sub>4</sub> + 1 mM KCl + 10  $\mu$ M MPS. The MPS adlayer was mostly disordered.

discerned by atomic-resolution STM imaging. The admittance of MPS into the STM cell resulted in immediate changes at the Pt(111) electrode, reflecting fast adsorption kinetics of MPS molecules. Figure 2b provides a close-up view of a terrace, showing poorly organized protrusions and clusters. All protrusions were associated with irreversibly adsorbed MPS admolecules on the Pt(111) electrode, which barely changed with the modulation of potentials between 0 and 1.0 V. Even into the potential region where hydrogen evolved, MPS remained intact. These results support the notion of strong adsorption of MPS on the Pt(111) electrode, much stronger than MPS/Au(111) and Cu(111).<sup>17,19,20</sup>

Although molecular ordering of MPS at this electrified interface is lacking, a higher resolution STM scan discerned each MPS admolecule as a single spot. Two neighboring spots were separated from each other at 0.48 nm [the intermolecular spacing in the Pt(111)] ( $\sqrt{3} \times \sqrt{3}R30^\circ$  structure, frequently observed with organosulfur compounds adsorbed on Pt(111) between 0.1 and 0.3 V in 0.1 M HClO<sub>4</sub>. This 0.48 nm nearest-neighboring spacing could be too small to allow MPS molecules to lie parallel to the Pt(111) surface. It is likely then that the MPS molecules were tethered to the Pt(111) surface by their sulfur head groups, while the sulfonate end groups were pending in the solution. This adsorption configuration could prevail from 0 up to 0.3 V. Increasing the potential in excess of 0.3 V, however, did not produce an ordered molecular structure. In comparison, the MPS molecules underwent a disorder-to-order phase transition, yielding a structure of Au(111):  $(9 \times \sqrt{3})$ , when the potential was made more positive than 0.67 V.<sup>19</sup> Meanwhile, the adsorption of MPS on Cu(111) was proved to be disordered by STM.<sup>17</sup> Consequently, the interaction between the MPS molecule and the metallic electrode varied substantially.

The disordered MPS adlayer on Pt(111) seen in perchloric acid could not be converted to an ordered one by varying the concentration or potential. The adsorption of MPS, compared with the hexanethiol and benzenethiol molecules adsorbed on Pt(111),<sup>27,28</sup> could involve different intermolecular interactions between MPS admolecules. These interactions could play bigger and more complicated roles in guiding the arrangement of MPS admolecules than those in typical alkanethiol adlayers, notwithstanding the fact that the S-Pt bond is particularly strong and a threefold coordination is greatly favored. The intermolecular interactions could be hydrogen bonds, involving MPS admolecules and their neighbors or those in the solution and ion pairing between  $Cu^{2+}$  and  $SO_3^-$  of MPS. We postulate that these intermolecular interactions could be more intricate than the van der Waal interactions predominating in alkanethiol or arylthiol monolayers.<sup>27,28</sup> These intermolecular hydrogen bonds could drive molecular aggregates observed on the Pt(111) electrode (Fig. 2).

Electrodeposition of Cu on MPS-modified Pt(111).- We brought the potential stepwise from 0.8 to 0.1 V to implement Cu deposition. When the potential was switched from 0.3 to 0.2 V, the Pt(111) electrode, as seen with the STM, changed dramatically. Blotches of Cu deposit surged throughout the whole electrode, as shown by the STM images in Fig. 3. Most blotches have circular perimeters with an average diameter of 3.0 nm, and frequently they were diatomic in height. Once the Cu<sup>2+</sup> species in the tip-electrode gap were depleted, surface morphology stabilized until the potential was changed to a more negative value. In situ STM showed that continuous Cu deposition produced big chunks of Cu next to the imaged area. Evidently, Cu deposition proceeded in a threedimensional (3D) mode on a Pt(111) electrode modified with an MPS adlayer. The evolution of the morphology of the Cu deposit has been studied using theoretical models detailing the diffusion and nucleation rates.<sup>3</sup>

Metallization at the alkanethiol-modified electrode has been extensively examined, showing that metal adatoms could be deposited at the top or at the bottom of the thiol monolayer, depending on the chemical identity of the adatom, the structure of thiol molecules, and the overpotential used to drive the reduction.<sup>31-34</sup> In MPS/Pt(111),



**Figure 3.** (Color online) In situ STM images showing the surface morphology and 3D islands of Cu deposited on MPS-modified Pt(111) in 0.1 M HClO<sub>4</sub> + 1 mM Cu(ClO<sub>4</sub>)<sub>2</sub> + 1 mM KCl + 10  $\mu$ M MPS. The potential of Pt(111) was fixed at 0.2 V, whereas the imaging conditions were 100 mV bias voltage and 1 nA feedback current. Images in (a) and (b) were collected in a time difference of 20 min.

the admolecules were adsorbed so strongly that it would be difficult for the Cu deposit to displace the MPS adlayer. In addition to the possibility of being deposited on the MPS adlayer, Cu adatoms could also penetrate the MPS adlayer and were deposited close to the sulfur end of the MPS molecule. These Cu adatoms then served as nucleation sites for further Cu deposition, leading to the 3D islands of Cu on Pt(111). Small Cu islands grew in size with time and eventually coalesced to form larger Cu chunks. The strongly held MPS molecules could be buried under the Cu deposit. Given the rough surface morphology of the Cu deposit produced on the MPSmodified Pt(111), an electrolyte could be trapped in the Cu film, a clearly undesirable situation.

The structure of MPS adlayer on Pt(111) precoated with a monolayer of Cu atoms.— To further explore the adsorption of MPS molecules, we considered the Pt(111) electrode first modified with Cu adatoms. This was achieved in 0.1 M HClO<sub>4</sub> + 1 mM Cu(ClO<sub>4</sub>)<sub>2</sub> by holding the potential of Pt(111) at 0.35 V, the negative end of the UPD process. According to previous studies, this would produce a full monolayer of Cu adatoms on the Pt(111) electrode.<sup>24,26</sup> A mixed solution of perchloric acid +10  $\mu$ M MPS +1 mM KCl was then admitted into the STM cell with this Cu-modified Pt(111) electrode potentiostated at 0.35 V. The addition of MPS almost immediately yielded patches of ordered arrays, as shown in Fig. 4a. The internal molecular arrangement of this structure is detailed by the STM image shown in Fig. 4b.

The unit cell of this ordered array, outlined by the white line, appears to be rectangular with two edges measured with 1.1 and 0.96 nm lengths in the directions of  $\langle 110 \rangle$  and  $\langle 121 \rangle$  of the Pt(111) surface, thus indicating a (4  $\times$  2  $_{\rm V}$  3)rect structure. A close inspection of these STM images reveals a distinct zigzag pattern along the  $\langle 121 \rangle$  directions of the Pt(111) surface, resulting from skewing of the middle MPS molecule to the shorter edge. The shortest distance between MPS molecules was  $\sim 0.6$  nm, which is much larger than the ideal value of  $\sim 0.24$  nm reported for the disulfide structure seen on the Au(111) surface.<sup>35</sup> Thus, this zigzag arrangement was not due to the formation of a disulfide linkage between two neighboring MPS molecules. Essentially, there were two pronounced protrusions ascribable to MPS admolecules in the cell, yielding a coverage of 1/16 or 0.125. Because of the longer intermolecular spacing, 0.6 vs 0.48 nm seen with MPS adsorbed on Cu-coated and bare Pt(111), there were less MPS molecules adsorbed on the Cu-decorated Pt electrode than on the bare Pt electrode. In addition to these features, two weaker spots were also imaged by the STM. Because these features were only 0.3 nm to the MPS molecule in the middle of the cell, these spots could be the coadsorbed chloride anions, rather than the MPS admolecules.

A ball model is shown in Fig. 4c to account for this  $(4 \times 2 \sqrt{3})$  rect structure with the MPS molecules adsorbing upright at the threefold hollow sites on Pt(111), which agrees with the equal corrugation heights seen for all the MPS molecules by the STM. The readiness to form ordered MPS molecular arrays on Cu/Pt(111) con-



Figure 4. (Color online) [(a) and (b)] Molecular-resolution STM images revealing the structure of MPS adlayer deposited on Pt(111) precoated with a monolayer Cu adatoms. The potential of Pt(111) was held at 0.35 V in 0.1 M HClO<sub>4</sub> + 1 mM KCl + 10  $\mu$ M MPS, where a monolayer of Cu adatoms likely arranging in a pseudomorphic structure was electroplated on the Pt(111) electrode. This structure is designated as (4 × 2  $\sqrt{3}$ )rect, which could contain chloride anions, as indicated by the ball model shown in (c).

trasts sharply with the largely disordered adlayer on bare Pt(111), although these results were all obtained in strongly acidic media and in the presence of chloride, where intermolecular hydrogen bonds could form, as mentioned earlier. It is possible that coulombic interactions between the sulfonate group of MPS and  $Cu^{2+}$  could prevail to produce the ordered MPS structure on the Cu/Pt(111) electrode. It is not clear if chloride anion was crucial in this structure. We are conducting STM imaging experiments of MPS on Cu/Pt(111) in the absence of chloride to resolve this issue.

The adsorption of methanethiol and octanethiol on Cu(111) has been examined in an ultrahigh vacuum, <sup>36-38</sup> revealing a zigzag molecular arrangement rather similar to the STM results observed here in this study. In the intermediate honeycomb phase and the more stable pseudo-(100) phase of the methanethiol and octanethiol molecules, the Cu(111) substrate is shown to reconstruct into a squarelike (100) network at room temperature. This adsorbate-induced reconstruction of Cu(111) did not seem to occur in the present structure of MPS/Cu/Pt(111) because the (4 × 2  $\sqrt{3}$ )rect MPS structure seen here differs from those found in vacuum.<sup>36,37</sup>

This is not surprising because potential control in electrochemistry frequently results in interfacial structure very different from that in the vacuum. For example, sulfur adatoms were found to form Cu(111),  $(\sqrt{3} \times \sqrt{3})R30^{\circ}$  and  $(19 \times 19)$  in electrochemistry,<sup>39-41</sup> which are not seen in vacuum. Certainly, the Cu UPD layer on Pt(111) was structurally and electronically different from Cu(111). However, according to previous studies of UPD on Pt(111), Cu adatoms form a pseudomorphic structure on Pt(111).<sup>24,26</sup> It is not clear, however, if the Cu structure persisted upon the adsorption of MPS admolecules. It is possible that Cu adatoms rearranged to a more stable configuration with MPS admolecules to produce the (4  $\times 2 \sqrt{3}$ )rect structure seen by the STM. It is, however, made clear that the Cu UPD layer was not displaced by MPS admolecules.



**Figure 5.** (Color online) Time-dependent in situ STM images showing the 20 min continuous deposition of Cu on Pt(111) premodified with a monolayer of Cu adatoms. The potential was held at 0.1 V in 0.1 M HClO<sub>4</sub> + 1 mM Cu(ClO<sub>4</sub>)<sub>2</sub> + 1 mM KCl + 10  $\mu$ M MPS. Roughly five layers of Cu were electroplated on the Pt(111) electrode. These STM results show that Cu deposition proceeded mainly in a layer manner, producing Cu flakes with an average height difference of 0.21 nm.

Multilayer Cu deposit on Pt(111) precoated with a Cu monolayer.- We then proceeded to plate more Cu by shifting the potential negatively from 0.3 to 0.1 V. The time-dependent STM images shown in Fig. 5a-c illustrate the processes of Cu deposition on Pt(111) already decorated by a monolayer of Cu adatoms. Compared with the prominent 3D growth of Cu islands on MPS-modified Pt(111), the Cu deposit was distinctively flakelike with poorly defined perimeters, but more importantly with clear layer features. Judging from the difference in height ( $\Delta z = 0.21$  nm) of most patches, each flake is attributed to a monolayer of Cu deposited on top of another Cu layer. Thus, copper deposition proceeded mostly in a layered manner under the present conditions. The copper flakes expanded laterally with time, while new Cu seeds nucleated. The MPS admolecules adsorbed on the copper deposit could either reduce the rate of copper reduction or increase the rate of Cu diffusion on the Pt electrode. These conditions are thought to favor the twodimensional growth of the Cu deposit.<sup>3</sup>

Switching to higher resolution STM scans discerned the molecular structure on the Cu deposit. Figure 6a is acquired in a region where monolayer and bilayer Cu deposits coexisted, as indicated by the difference in the corrugation heights ( $\Delta z = 0.21$  nm) of different domains. The ordered arrays seen in the darker region are associated with the (4  $\times$  2  $_{\rm V}$  3)rect structure residing on a monolayer Cu. The higher terrace nearly occupying the whole upper image in Fig. 6a was due to the bilayer Cu deposit, on which some ordered structures were also imaged. Although this new structure was not seen clearly in this image, some striped patterns were imaged by the STM. The protracted STM imaging was able to discern the internal molecular structures formed on the multilayer Cu deposit. For example, the STM image shown in Fig. 6b was obtained with about five layers of Cu deposits, showing locally ordered MPS structures. It seems that the MPS floated atop the Cu deposit, rather than being buried underneath under the present deposition conditions.

As revealed by the high resolution STM scan shown in Fig. 6c, the MPS molecules appeared to arrange in an ordered form, al-



**Figure 6.** (Color online) High resolution STM images revealing the structures of MPS admolecules deposited on multilayer of Cu deposited on Pt(111) precoated with a Cu UPD layer in 0.1 M HClO<sub>4</sub> + 1 mM Cu(ClO<sub>4</sub>)<sub>2</sub> + 1 mM KCl + 10  $\mu$ M MPS. MPS molecules adsorbed on the first and second layers of Cu are seen in (a), where those residing on multilayer Cu are observed in (b) and (c).

though the degree of ordering was not as good as those of (4  $\times$  2  $\sqrt{3}$ )rect found at the Cu monolayer. Rows of MPS admolecules ran parallel to the main axes of the Pt(111) surface, and two neighboring molecules were 0.52 nm apart, suggesting a  $(2 \times 2)$  structure. Compared with the mostly disordered MPS adlayer on Cu(111),<sup>17</sup> our present STM results nonetheless indicate ordered MPS adlattice on the multilayer Cu deposit, despite the high density of defects. Overall, the surface morphology of the Cu deposit is much smoother than that seen in Fig. 3. The Cu deposit could be more compact than that deposited directly on the MPS-modified Pt(111) electrode. In other words, the Cu film deposited on Pt(111)preconditioned by a Cu monolayer would contain less defects than that formed on MPS-modified Pt(111). These results suggest the important role of the atomic structure of the Cu deposit onto which MPS molecules were adsorbed, and the Cu deposit nucleated and grew subsequently.

#### Conclusions

The structures of MPS molecules adsorbed on a Pt(111) electrode have been examined by molecular-resolution STM, showing that the arrangements of MPS molecules varied greatly with the surface state of the Pt(111) electrode. While the MPS adlayer was mostly disordered on pristine Pt(111) in 0.1 M perchloric acid, a highly ordered array of  $(4 \times 2 \sqrt{3})$  rect was discerned on a Cu-coated Pt(111) electrode. Cationic copper species could pair with the sulfonate group on the MPS admolecules on the Cu/Pt(111) electrode. The contribution of chloride coadsorption to the ordered structure is unclear now. The adsorption of an MPS adlayer on Pt(111) exerted a marked influence on the deposition of Cu, which produced 3D islands of Cu distributing statistically on the Pt electrode. In contrast, the deposition of Cu on a Pt(111) electrode preconditioned with a Cu adlayer resulted in layered-type growth, as STM imaging revealed atomically flat flakes with a height difference of 0.21 nm. In situ STM imaging revealed an ordered (2  $\times$  2) MPS structure on most Cu flakes compared with the  $(4 \times 2 \sqrt{3})$  rect structure found on a monolayer of Cu. MPS molecules could be floating, rather than being buried by the Cu deposit. The as-produced Cu film appeared to be smooth and well packed on the Pt(111) electrode. This study suggests that the atomic structure of the Cu deposit could be important to the adsorption of MPS molecules and the subsequent deposition of Cu.

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