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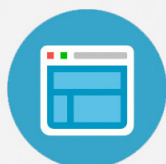
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Leveling effects of copper electrolytes with hybrid-mode additives

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100 nm vias were completely filled with copper for interconnect applications using an electrolyte in the presence of polyethylene glycols (PEG) and a hybrid-mode additive, benzotriazole (BTA). Electrochemical analyses indicated that BTA with a higher concentration inhibited the copper deposition rate, whereas BTA with a lower concentration accelerated the copper deposition rate. This electrolyte thus generated an enhanced deposition gradient within a gap because the PEG molecules and the high concentration of BTA, adsorbed at the opening of the gap, inhibited the deposition. Meanwhile, a little BTA diffused into the inner part of the gap and thus accelerated the deposition of copper. Therefore, this two-component (PEG and BTA) additive electrolyte had the capacity of a three-additive bath (accelerators, suppressors, and levelers). © 2002 American Vacuum Society. [DOI: 10.1116/1.1517262]

I. INTRODUCTION

As demand increases for the electroplating of narrower interconnects with copper, new assemblages of additives must be developed. Organic additives added to copper electroplating baths can generally be categorized into accelerators, suppressors, and levelers. In earlier work, Reid and co-workers first proposed that two-additive electrolytes, contained only suppressors and levelers or only catalytic and suppressing molecular species, failed to fill sub-0.15 μm damascenes.^{1,2} Moreover, a strong bottom-up filling requires an electrolyte with a polymer suppressor, an accelerator, and certain levelers.³

However, plating baths that contain more classes of additives may increase the resistivity of copper films⁴ and increase the complexity of annealing processing. A possible approach to tackling the issue is to introduce a hybrid-mode additive, which can simultaneously cause acceleration and inhibition, replacing the original functions of an accelerator and a leveler in the three-additive electrolyte. The hybrid-mode additive has been discussed with respect to printed circuit boards (PCBs).⁵ Ogden and Tench reported⁵ that some additives at low concentrations, coordinate Cu^{2+} with its donor group ($-\text{SH}$ or $-\text{NH}_2$), and then form accelerating species of copper-complexed monomer species. In contrast, additives at higher concentrations form a dimer species and

their complexes form and behave as decelerating species. The representative chemistries of hybrid-mode additives are typically those of tautomeric forms, including mercapto groups, thione groups, N-S chelates, and diazo nitrogens of ring systems.⁵

The concentration of species at the bottom of the feature is lower than that at the shoulder of the feature because of the diffusion behavior of additives within the damascene structure. Consequently, the hybrid-mode additive can accelerate the deposition rate in the damascene base (a low-concentration region) as an accelerator component and can inhibit the deposition of copper at the opening of the features (a high-concentration region) as a leveler component. This work introduces the benzotriazole (BTA) additive as a hybrid-mode additive, owing to the structure of the diazo nitrogens in the ring system. An electrolyte results in the deposition of copper with a lower resistivity than that of copper films deposited by electrolytes with additives of mercapto groups or other disulfide groups,⁵ since BTA is free of S atoms.⁶ Furthermore, BTA is already an excellent corrosion inhibitor for copper surfaces.^{7,8} (For example, BTA is used in the CMP process.) This proposed electrolyte thus facilitates consistency with other processes.

II. EXPERIMENT

Copper electroplating experiments were carried out in a 267 ml Hull Cell.⁹ The copper anode was laid against the

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right-angle side and wafer fragments with a size of $1\text{ cm} \times 3\text{ cm}$ were used as a cathode and laid at the center of the sloping side. Contact to the fragments was made outside of the electrolyte with an alligator clip. Agitation air was introduced into the solution from a compressor. The basic electrolyte (BE) consisted of copper sulfate (30 g/L), sulfuric acid (150 mL/L), and chloride ions (100 ppm). All electroplating was performed at room temperature, and the dc bias current density was 1 mA/cm^2 . The patterned wafers consisted of a 30-nm-thick chemical-vapor-deposited (CVD) TiN layer as the diffusion barrier and a 200-nm-thick ionic metal plasma (IMP) deposited Cu film as the seed layer. The IMP technique promotes the transportation of Cu ions into the bottom of the via holes from the Cu plasma, improving the step coverage of the Cu seed layer in the damascene.¹⁰ Tafel polarization analyses and cyclic voltammetric stripping (CVS) measurements were taken to identify electrolytes with suppressing or accelerating species. In these analytical experiments, the counterelectrode was Pt and the working electrode was Cu or Pt, with a constant surface area of 0.5 cm^2 . All potentials are specified in relation to the Ag/AgCl electrode, which was used as the reference electrode. Dc polarization analyses were performed on an EG&G Potentiostat/Galvanostat model 273A and CVS measurements were obtained at room temperature by EG&G PARC model 616 RDE. In CVS analyses, the area under the stripping peak, A_s , corresponds to the charge required to oxidize the deposited copper and is proportional to the average deposition rate for that cycle.⁹ Additionally, the partially filled profiles of copper films were examined using field-emission scanning electron microscopy (FESEM).

III. RESULTS AND DISCUSSION

As described in Refs. 1 and 2, a bottom-up fill has two mechanisms: one mechanism is the three-additive model in which the suppressing polymer is combined with accelerators and levelers, and the other is the two-additive model in which the suppressing polymer is combined with levelers. Following West and co-workers,¹¹ we experimentally elucidated diffusion and inhibition effects of additives on gap-filling performance,¹⁰ and demonstrated the filling promoter, which consisted essentially of thiazole derivatives in which a benzyl group and an amino group ($-\text{NH}_2$) such as 2-aminobenzothiazole (2ABT), excellently fill the gaps of the 130 nm damascene.¹¹ For comparison, the PEG-Cl-2ABT bath was designated as the latter mechanism (two-additive model) and the PEG-Cl-BTA bath was denoted as the former mechanism (three-additive model). The hybrid-mode additive (BTA) with the chemical structure of the diazo nitrogens of the ring system acted as an accelerator or an inhibitor, depending on its concentration.

Figure 1 shows the filling evolutions of the PEG-Cl-BTA and PEG-Cl-2ABT baths for electroplating trenches/vias with feature sizes of 0.1, 0.12, 0.18, and $0.35\text{ }\mu\text{m}$; the plating times were 1, 5, and 10 s, respectively. For simplicity, the

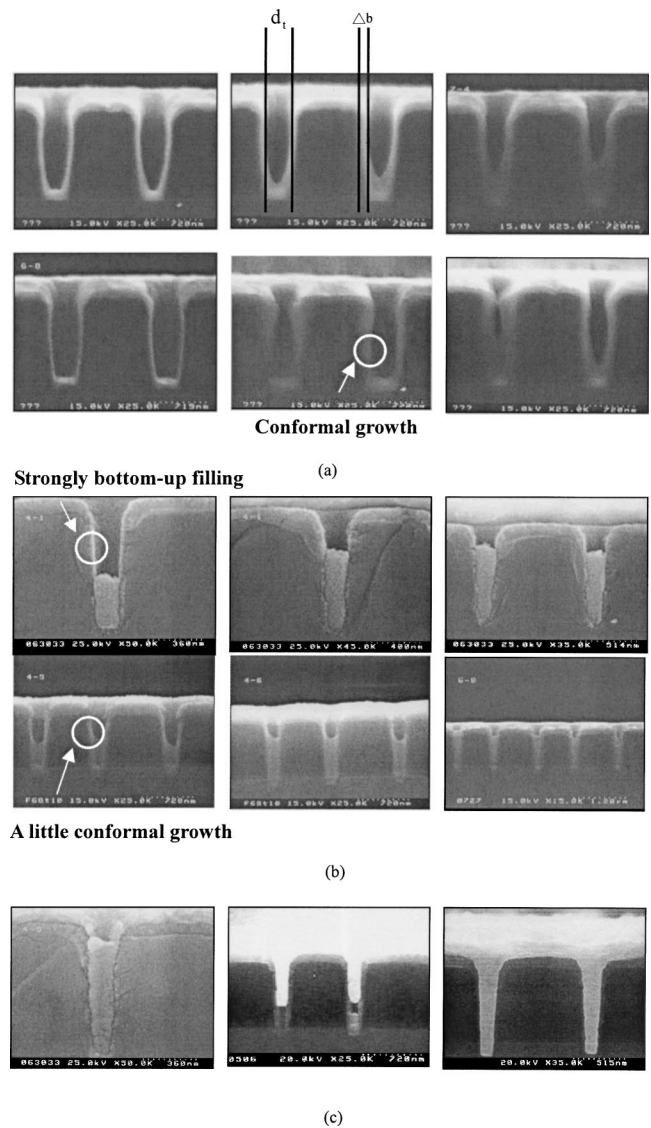


Fig. 1. Filling evolutions of two electrolytes used in electroplating trenches/vias with feature sizes of 0.1, 0.12, 0.18, and $0.35\text{ }\mu\text{m}$. PEG (40 ppm) and additives (50 ppm) were added to the basic electrolyte. (a) Upper plots: $0.35\text{ }\mu\text{m}$ patterns deposited by PEG-Cl-BTA baths; lower plots: PEG-Cl-2ABT baths with plating times of 1, 5, and 10 s. (b) Same experiments for $0.18\text{ }\mu\text{m}$ patterns with plating times of 1, 2, and 5 s. (c) Left plot: $0.12\text{ }\mu\text{m}$ pattern deposited by PEG-Cl-BTA baths; central plot: PEG-Cl-2ABT bath; right plot: $0.1\text{ }\mu\text{m}$ pattern deposited by PEG-Cl-BTA baths.

physical diameter of each via (d_e) was defined as a sum of a diameter, d_t , and double thickness of the conformal Cu deposition (Δb) on the sidewall:¹² $d_e = d_t + 2\Delta b$, as in Fig. 1(a). An analysis of the thickness of the conformal growth on the sidewall surface yields many interesting observations. First, for the $0.35\text{ }\mu\text{m}$ pattern shown in Fig. 1(a), apparent conformal growth of the 2ABT-containing electrolyte is observed (lower plots). The pattern filled by the BTA-containing electrolyte yielded a better bottom-up performance (upper plots) than the 2ABT. This phenomenon was more significant in the $0.18\text{ }\mu\text{m}$ pattern, shown in Fig 1(b): a strongly superfilling force was demonstrated in the BTA-containing electrolyte (upper plots); however, slightly con-

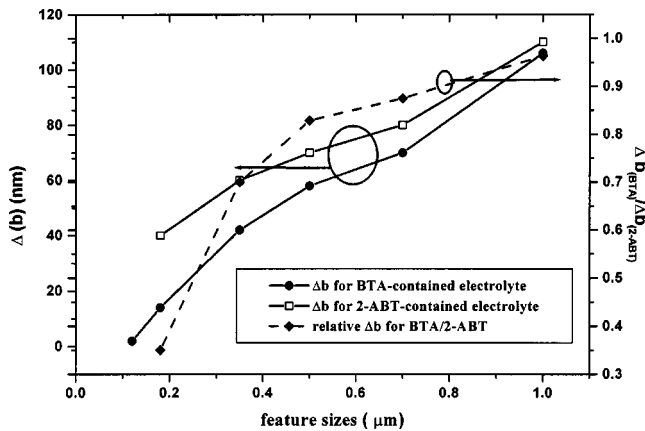


FIG. 2. Conformal thicknesses, Δb_{2ABT} , Δb_{BTA} , and $\Delta b_{BTA}/\Delta b_{2ABT}$ as a function of pattern size.

formal growth of the 2ABT-containing electrolyte (lower plots) was still observed. Second, the value of $\Delta b_{BTA}/\Delta b_{2ABT}$ was less than 1 and decreased as the features became narrower, as shown in Fig. 2. Restated, the capacity of the PEG–Cl–BTA bath for bottom-up growth was greater than that of the PEG–Cl–2ABT bath, especially for the narrower damascene. In Fig. 2, Δb values were calculated for a specified plating time, when the bottom-up filling was observable. Consequently, for the filled $0.1 \mu\text{m}$ patterns shown in Fig. 1(c), the PEG–Cl–2ABT bath failed to fill the vias (central plot); in contrast, the PEG–Cl–BTA bath was still effective (left plot). The transient filling behaviors suggested that the filling capacities of BTA solutions exceeded those of 2ABT solutions. Finally, the thickness, Δb , of the conformal growth of both electrolytes decreased as the features shrank, as shown in Fig. 2. As reported, the transient filling behavior of the two-additive electrolyte (organic disulfide and polymer additive) followed two-step mechanisms: step (1) conformal filling, followed by step (2) bottom-up filling.¹³ A dense film with a polymer–chloride complex, first formed on the sidewall of the trench, contributed to the conformal growth of the deposited copper. To the authors' knowledge, the mass transfer of PEG molecules into smaller features becomes more difficult, leading to a less conformal growth at the sidewall.^{2,13} Consequently, adding a leveler, such as 2ABT, into the electrolyte can prevent the formation of a seam at the opening of the feature, since PEG–Cl has less effect on smaller features. However, adding an accelerator, such as BTA, to the electrolyte can further enhance bottom-up growth when the surface coverage of PEG is lower for smaller features.

2ABT and BTA as additives responded to filling dynamics that were different from partially filled profiles. However, more sophisticated experiments are required to verify these chemical's electrochemical properties. The deposition gradient of an electrolyte within the damascene was evaluated by measuring Tafel polarization curves of electrolytes with and without PEG, as shown in Fig. 3(a), because of the minimal

effect of PEG at the bottom of the damascene. The inhibitive capacity of copper deposition from the PEG–Cl–2ABT electrolyte (curve 3) exceeds that of the Cl–2ABT electrolyte (curve 2), because of the suppressive effect of the polymer–chloride complex. Without PEG in the electrolyte, even adding 10 ppm 2ABT into the Cl–2ABT bath inhibits the deposition of copper (curve 7), as compared to the deposition with the basic electrolyte bath (curve 1). In addition, the suppression effect of copper deposition by 2ABT increased with its concentration of 2ABT, as shown in Fig. 3(b). Therefore, 2ABT actually inhibited the copper deposition.

By comparison, a high BTA concentration in the PEG–Cl–BTA bath resulted in stronger inhibition than with 2ABT additives, as determined by comparing curve 2 with curve 4, and curve 3 with curve 5 in Fig. 3(a). However, copper deposition from a Cl–BTA electrolyte with a BTA concentration of around 10 ppm [curve 6 in Fig. 3(a)] was accelerated over that of the basic electrolyte bath [curve 1 in Fig. 3(a)]. Therefore, whether the hybrid-mode BTA additive accelerates or suppresses the deposition of copper depends strongly upon the amount of BTA species added, as shown in Fig. 3(c). Based on those data in Fig. 3(a), the deposition gradient (curve 5 in relation to curve 6) with pattern depth for the BTA-containing electrolyte was significantly larger than that of the 2ABT-containing electrolyte (curve 3 in relation to curve 7). Consequently, the bottom-up enhancement of BTA was expected to be greater than that of 2ABT.

Figure 4(a) shows CVS data for BTA concentrations of 0, 10, and 40 ppm. These data show that the rates of deposition, D_{BTA} , of the electrolytes with those BTA concentrations (determined from the area of the stripping peak) are in the following order: $D_{BTA}(10 \text{ ppm}) > D_{BTA}(0 \text{ ppm}) > D_{BTA}(40 \text{ ppm})$. Additives are transported only by diffusion because the damascene structure is very small. Therefore, the static stripping peak area, calculated from CVS spectra, truly specifies that the deposition processes are accelerated or inhibited by additives. Figure 4(b) plots the normalized static stripping area, A_s , which is the ratio of the area of the stripping peak, obtained for various concentrations, to the stripping peak area without additives. Figure 4 shows that the Cl–BTA bath was involved in two mechanisms. BTA acted as an accelerator ($A_s > 1$) at lower concentrations but as a leveler ($A_s < 1$) at higher concentrations. With reference to a previous report,⁵ two donor groups ($-\text{NH}_2$) of additives that can coordinate Cu^{2+} or accelerating species of the copper complexed monomer species were formed at lower concentrations of BTA. In contrast, at higher concentrations, a dimer species and its complexed form, were generated as the decelerating species. The chemical structure of BTA additive matched that of the diazo nitrogens in the ring system, demonstrating the behavior of a hybrid-mode additive. However, the inset in Fig. 4(b) shows that A_s for 2ABT was always smaller than 1, indicating that 2ABT acted as a leveler. The CVS analyses are consistent with the results of the Tafel polarization (Fig. 3). The CVS curves for Cl–2ABT and Cl–BTA baths show that A_s depends linearly on the inhibiting region. This linear relationship between A_s and levels of

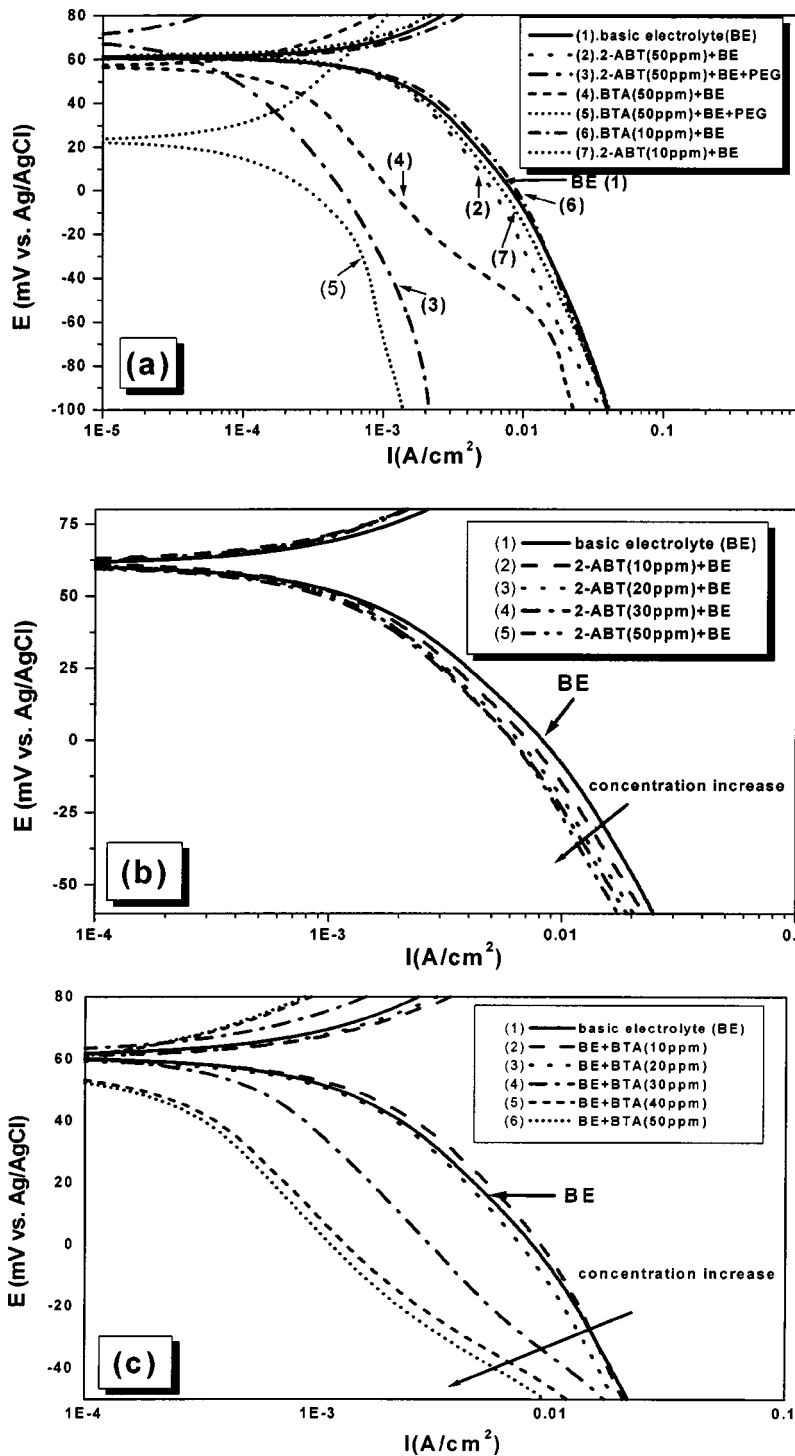


FIG. 3. Tafel plots for Cu electroplating using various electrolytes. (a) Basic electrolyte, PEG–Cl–BTA, PEG–Cl–2ABT, Cl–BTA, and Cl–2ABT baths. (b) Various concentrations of 2ABT additives added to the basic electrolyte. (c) Various concentrations of hybrid-mode BTA additive added to the basic electrolyte.

levelers follows the Langumir isotherm,¹⁴ such that an increase of the concentration of the leveler linearly enhances the surface coverage of organic additives, decreasing the rate of deposition. This observation also explains the Tafel polarization curves with BTA and 2ABT additives.

An analysis of the Tafel polarization and CVS measurements shows that the excellent superfilling behavior of the PEG–Cl–BTA bath can be attributed to the superior deposition gradient within the damascene, since, at the bot-

tom of the damascene, Cl–BTA catalyzed the bottom-up deposition, whereas PEG–Cl–BTA was more strongly inhibitive than the PEG–Cl–2ABT bath around the damascene opening. Deposition is void free for 100 nm vias with an aspect ratio of 10:1, as shown in Fig. 1(c) (right plot) because the BTA–PEG–Cl bath has a stronger bottom-up filling capacity for small features. The as-deposited Cu film offers a gap-filling advantage and has a resistance as low as 2.3 $\mu\Omega$ cm.

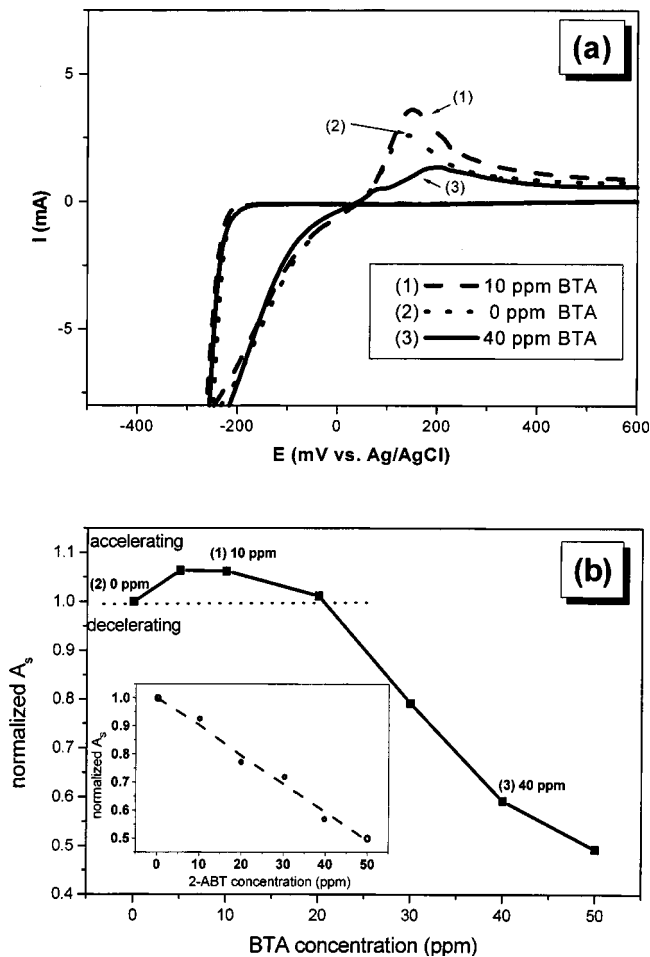


FIG. 4. (a) CV measurements for various concentrations of BTA additives added to basic electrolytes. (b) Normalized stripping area A_s measured by CV for various concentrations of 2-ABT and BTA additives added to basic electrolytes.

IV. CONCLUSIONS

The hybrid-mode additive, BTA, which can simultaneously cause acceleration and inhibition, replacing the original functions of an accelerator and a leveler in the three-

additive electrolyte, was demonstrated. An electrolyte with BTA and PEG successfully electroplated 100 nm vias with an aspect ratio of 10:1. BTA at a low concentration level acted as a bottom-up accelerator and increased the rate of deposition at the base of the vias. BTA at a high concentration acted as an effective leveler and enhanced the inhibition of the PEG suppressor at the opening of the vias. Using an electrolyte with the hybrid-mode additive yields a higher deposition gradient within the filled patterns than another recipe that includes only suppressing agents. The filling capacity within deep submicron damascenes obtained by using this combination of additives is valuable for use in new generation devices.

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