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# Investigation of EUVL Reticle Capping Layer Peeling under Wet Cleaning

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## ABSTRACT

In the absence of a pellicle, an EUVL reticle is expected to withstand up to 100 cleaning cycles. EUVL reticles constitute a complex multi-layer structure with extremely sensitive materials which are prone to damage during cleaning. The 2.5 nm thin Ru capping layer has been reported to be most sensitive to repeated cleaning, especially when exposed to aggressive dry etch or strip chemicals [1]. Such a Ru film exhibits multiple modes of failure under wet cleaning processes. In this study we investigated the Ru peeling effect. IR-induced thermo-stress in the multi-layer and photochemical-induced radical attack on the surface are investigated as the two most dominant contributors to Ru damage in cleaning. Results of this investigation are presented and corrective actions are proposed.

**Keywords:** ultraviolet, ruthenium damage, contaminants, radicals, thermal stress, mask cleaning, EUVL.

## 1. INTRODUCTION

EUV technology uses light reflected from the photomask surface rather than light transmitted through the substrate, which changes the photomask nature of the imaging process onto the wafer level from transmissive to reflective. Presently, no pellicles are available for EUV masks to protect the pattern side from contamination during storage, use or transport. This implies that EUV masks are more exposed to contamination than optical masks, and thus it is expected that EUVL masks will need to undergo more cleaning cycles during their useful life in order to maintain high device production yields. During mask manufacturing, ionic and organic contaminations are likely to be detected within the final inspection step; furthermore, shipping and handling can also lead to additional particle deposition. EUV reticle handling in wafer fabs includes storage, inspection, transfer to the scanner vacuum and positioning onto the electrostatic-clamp stage, thereby exposing the reticle to the risk of added particles as well as ionic and organic contamination. In addition, a thin film of carbon may grow as the reticle is exposed to EUV radiation during use. All the EUV mask composing layers (Absorber, Capping layer, Mo/Si Multilayer) must be properly preserved during multiple cleaning cycles and exposure processes. Therefore, it is crucial to understand the effect of cleaning and exposure processes on EUV mask quality and printing performance. In this paper, we review the historical observation of the damage, individuate possible root causes for the damage, and propose hardware corrective actions to overcome this issue.

## 2. BACKGROUND

Particle deposition and carbon growth usually happens during handling, storage, use and exposure; these have great impact on EUV reflectivity, CD shift, pattern fidelity, lithographic stability and total mask life time. Along with these effects, ruthenium degradation is often observed in the form of oxidation to volatile RuO<sub>4</sub> oxide formation [2]. The latter effect has the most dramatic impact on mask lifetime.

Early attempts to deploy conventional mask cleaning technologies, such as SPM (sulfuric acid / hydrogen peroxide mix) or DIO<sub>3</sub> (DI-water + ozone) for removal of resist or other organic contamination as well as APM (ammonium hydroxide / hydrogen peroxide mix) for support of particle removal in physical force cleaning steps have failed due to their negative impact on EUVL functional layers and high risk of residual ions being transferred into the scanner's vacuum environment. Therefore, an in-situ UV (IUV) process has been developed, which leads to highly reactive hydroxyl radicals, hence to a highly efficient resist strip and final cleaning process [3,4]. If properly designed, an IUV process does not allow oxidizing agents such as DIO<sub>3</sub> to come in contact with the mask surface. The process is completely acid-free, and thin organic layers, including EUVL-induced carbon deposition, can be removed utilizing DI-CO<sub>2</sub> only. This provides for a completely waste-free chemical—so called green—process. In-situ UV has shown dramatic benefits for the most critical mask parameters, not only for EUVL, but also for 193i masks. Among these benefits are reduced ARC damage on COG, reduced CD shift on chrome, reduced overlay shift, reduced Ru layer damage, and increased resist strip rate [4].

Historically, IUV results obtained on EUVL blanks did not show damage to the Ru layer; surface roughness measurements did not show surface roughening, and very efficient carbon contamination removal was achieved after one clean. Reflectivity measurements are shown in Figure 1 and do not show reflectivity changes after 10 [5].

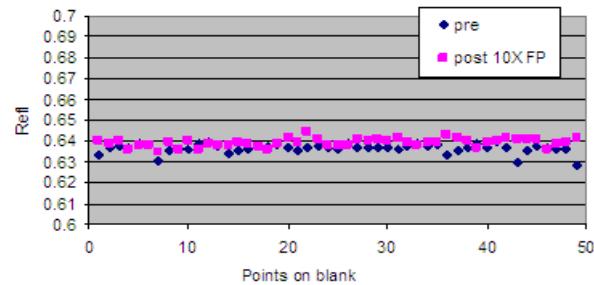


Figure 1: Comparison of reflectivity values on 49 locations on a EUV mask blank before and after 10 cleanings. Little to no change in reflectivity is observed [5].

Running the same qualified cleaning process on a patterned surface (EUVL mask) the results achieved are significantly different. Figure 2 shows roughness values obtained after multiple cleaning processes of an EUVL mask (total number of cleaning processes is 32x) [6].

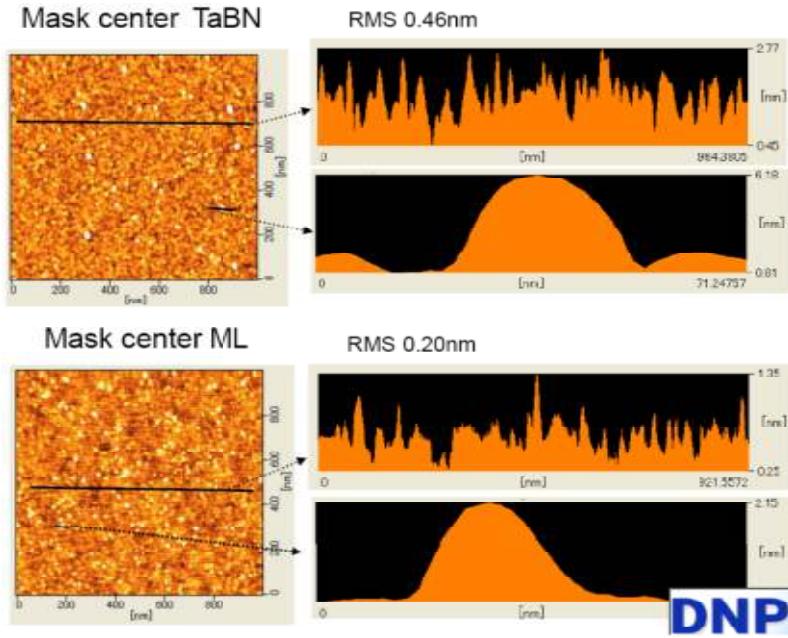


Figure 2. Roughness profiles of a mask, recorded after 32 consecutive cleaning processes in the center of the EUVL mask on a TaBN and ML surface. Analysis showed some nanometer-high bumps after the treatment.

The SEM analysis showed some surface damage occurred after 32 cleans, in the form of nanometer scale bumps [6].

In 2011, a EUVL mask from a different vendor was also investigated for its printing quality stability after consecutive cleaning processes. Interestingly, the results showed a significant change in the printed CD values on wafer level after 10 cleans of the EUV mask (Figure 3, left). This printing performance change is also correlated to surface damage, which was observed with SEM microscopy as well (Figure 3, right).

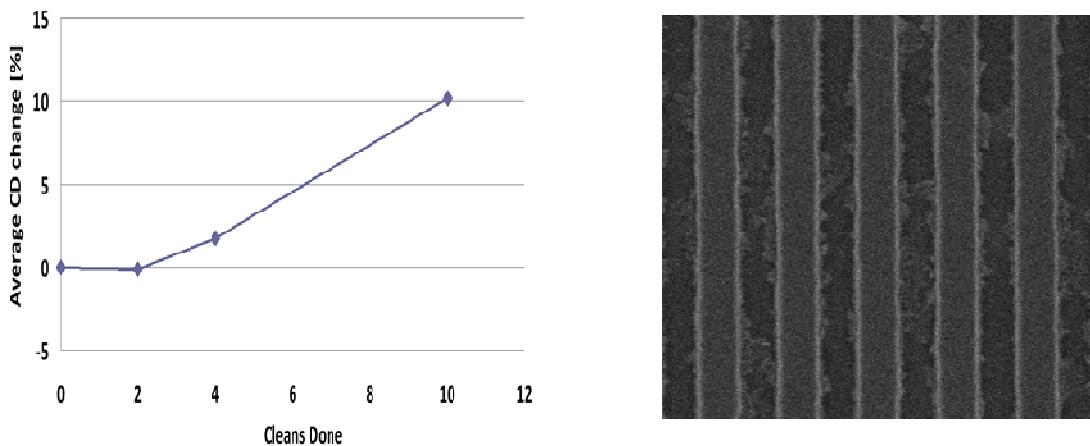


Figure 3. Average relative CD change in printed CD on wafer level after cleaning the mask a total of 10 times; a majority of these changes occur between 4th and 10th cleaning process of the EUV mask (left); evidence of Ru peeling at the interface between absorber and capping layer (right).

The damage becomes even more evident at the interface between absorber and Ru capping layer. The observation of differences in cleaning damage depending on mask vendor origin, indicates a strong influence of the mask manufacturing process. In particular, the absorber etch process has been reported to play a major role in the stability of the Ru layer during cleaning [7].

Nevertheless, based on a series of screening experiments we determined that the IUV process was also contributing to accelerated damage of the Ru layer. In those screening experiments we determined two potential mechanisms for Ru damage: photochemical erosion and thermal stress.

## 2.1 Photochemical Erosion

The emission spectrum of a medium pressure Hg lamp typically shows two main emission peaks at 185 nm and 254 nm. Depending on the quartz lamp bulb used, the 185 nm emission can be partially or totally absorbed; in the case of Suprasil Quartz, the transmission of the 185 nm line is about 90% (see #1 in Figure 4). Furthermore, the lamp bulb is isolated from the media flow by an additional (outer) quartz tube, whose optical properties affect the UV transmitted into the media and onto the surface.

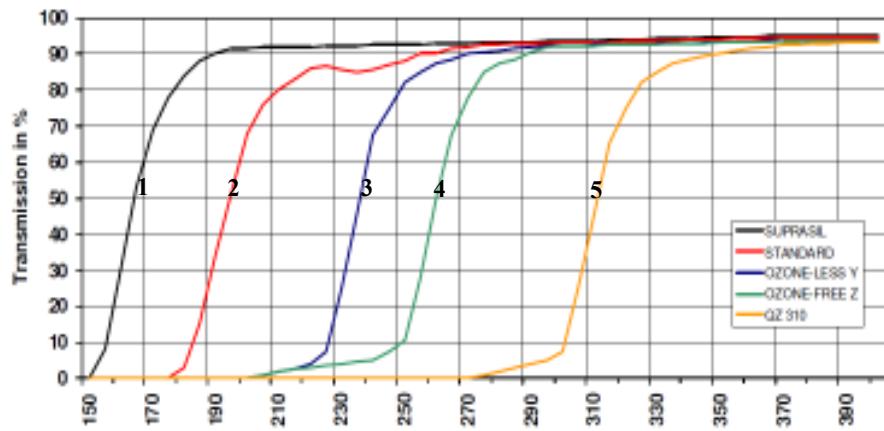
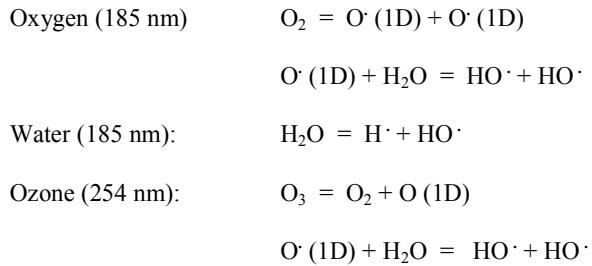
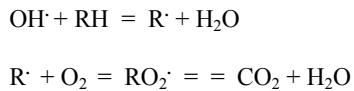


Figure 4. Different quartz transmission spectra in the UV range [8]; Suprasil (curve #1) transmits about 90% of the 185 nm emission line of a mercury gas emission spectra.

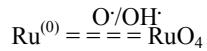
The IUV system producing the reported Ru damage results employed Suprasil for the medium pressure Hg emitter bulb and lamp housing, so that both 185 nm and 254 nm emissions could reach the media. In a typical cleaning process, ozonated water, or CO<sub>2</sub> water is used. At these wavelengths such media (oxygen, water and ozone) lead to photolysis, with generation of highly reactive singlet oxygen (O (1D)) and hydroxyl radicals [9]:



Hydroxyl radicals are usually responsible for organic removal from the surface; the reaction mechanism is known as hydrogen abstraction and produces organic radicals R· which in turn attach molecular oxygen to lead to peroxy radicals that undergo consecutive oxidation reactions to water and carbon dioxide:



Singlet oxygen and/or hydroxyl radicals could be responsible of Ru oxidation [10]:



## 2.2 Thermal Stress

The visible/near-IR emission spectrum of a medium pressure Hg lamp is shown in Figure 5.

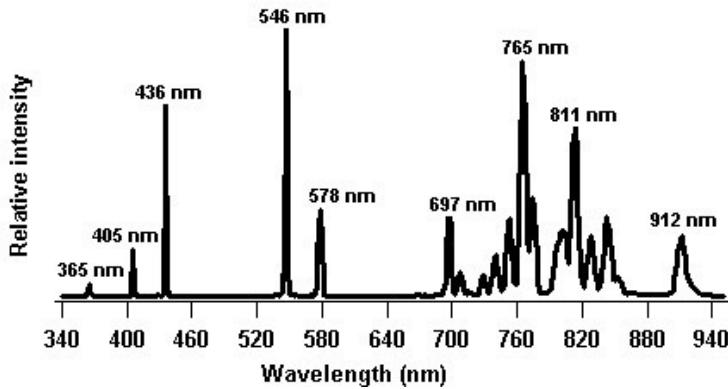


Figure 5. Visible/near IR spectrum of argon-doped medium pressure Hg lamp; the 912 nm emission in this spectral range has high contribution to heat [11].

A number of emission intensity peaks are visible in the near infra-red (IR) region of the spectrum; the 912 nm emission being the main contributor to the local emitted heating radiation. This contribution is usually enhanced by the presence of argon dopants inserted in the gas mixture of the medium pressure lamps. Due to the emitted heat from the lamp, and since the IUV arm is scanning across the mask surface continuously, the mask surface is subjected to thermal heat waves up to 50 times during a standard cleaning recipe. The largest thermal stress occurs at

the interface of absorber and capping layer material, since the thermal expansion coefficients of both materials are different (see Table 1).

Material	Thermal Expansion Coefficient [K <sup>-1</sup> ]
TaBN	3.6 - 5.2*10 <sup>-6</sup>
Ru	5.1 - 9.6*10 <sup>-6</sup>
Si	Si 2.6 - 3.3*10 <sup>-6</sup>
Mo	Mo 5.2 *10 <sup>-6</sup>

Table 1. Expansion coefficients for the main components of an EUV mask. The mismatch of this material property is responsible for thermal stress at the interface between absorber and capping layer.

This mismatch in thermal expansion coefficients could justify the observations illustrated in Figure 4; the largest thermal stress is localized at the interface between the absorber and the capping layer.

### 3. EXPERIMENTAL SET UP

A low pressure mercury lamp was proposed as hardware solution addressing both damage root causes, the photochemical erosion and the thermal stress. The UV-Vis the emission spectrum for both, a medium and low pressure mercury lamp, is shown in Figure 6.

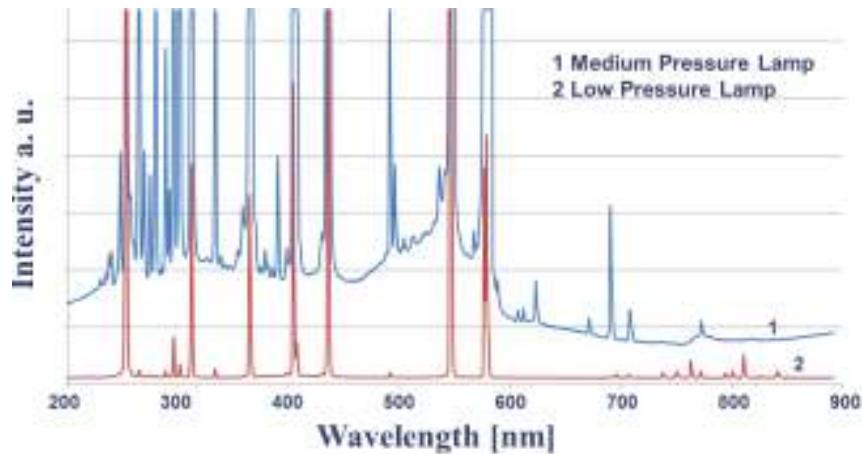


Figure 6: Emission spectrum of a low pressure (graph #2) and medium pressure (graph #1) mercury lamp between 200 nm and 900 nm; below 350 nm the emission spectrum of the low pressure mercury lamp shows fewer emission peaks compared to the medium pressure lamp.

Comparing the optical properties of the low pressure lamp to the medium pressure lamp, the following benefits become evident:

- 1) The UV region between 200 nm and 400 nm shows fewer emission peaks
- 2) The used quartz cuts-off emissions below 200 nm (not visible in Figure 7)
- 3) The strongest emission peak appears at 254 nm
- 4) IR emission is negligible

### 3.1 Experimental Conditions

The low-pressure Hg lamp was clamped on top of the extension module of the mask track cleaning tool; the experiments were conducted stationary (no chuck rotation) at a distance of 2 mm away from the lamp. Media flow was adjusted to 1.6 l/min and nitrogen flow at 6.5 l/min. A drying step was manually inserted at 500 rpm for 30 sec. EUV reflectivity measurements and SEM images were taken right after exposure of samples. The pattern mask was irradiated in two different areas of the reticle. Spectral measurements were taken with an OceanOptics Spectrometer USB2000.

## 4. RESULTS and DISCUSSION

### 4.1 Stripping Rate

In changing the type of mercury lamp (from high to low pressure) used for the IUV [1, 2] unit, we first reconfirmed the organic removal capability by conducting stripping experiments on resist (positive and negative) coated wafers. It is important to understand that with the low pressure mercury lamp no 185 nm emission peak is present, thus the photolysis of water and oxygen is not possible, which is the main chemical reaction mechanism utilized for an organic removal process.

A test bench was set up and experiments on both positive and negative coated photoresist wafers were conducted by using a media flow of pure water only. Four representative locations on the wafer surface were used for resist thickness measurements before and after the IUV treatment; Table 2 summarizes the stripping rate results.

Measured Area on Wafer	Stripped Resist (nm)	Stripping Rate(nm/min)
1	265	13,25
2	332	16,60
3	355	17,75
4	296	14,80

Table 2. Positive-tone resist stripping rates derived from measurements on four reference locations on the wafer surface.

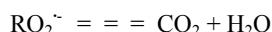
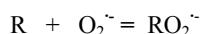
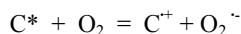
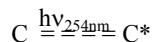
The stripping results favorably compare with or exceed the values achieved with a medium pressure lamp in the IUV unit, which are found as high as 10 nm/min [4]. The experiment result was confirmed with negative photoresist and the results are showed in Table 3.

Measured Area on Wafer	Stripped Resist (nm)	Stripping Rate(nm/min)
1	278	13,90
2	297	14,85
3	303	15,15
4	286	14,30

Table 3. Negative-tone resist stripping rates derived from measurements on four reference locations on the wafer surface.

#### 4.2 Photochemistry of Resist Stripping

The photochemistry of the process using an IUV unit with a low pressure mercury lamp is reviewed; due to the very low absorption coefficient of both water and oxygen at 254 nm, the irradiated UV light will hit the surface without significant intensity losses. At 254 nm, organic molecules have a maximum absorption which brings the carbon atoms to their excited state ( $C^*$ ); an electron transfer to molecular oxygen leads to a radical oxygen anion. This anion attacks the organic molecule radicals R leading to peroxy radicals ( $RO_2^-$ ) that undergoes consecutive oxidation reactions to  $CO_2$  and water. This reaction scheme can be summarized as follows: [7]



Each of these radical reactions competes with recombination; however, the intensity of the supplied light ensures enough radical concentration to get to organic oxidation to carbon dioxide and water.

#### 4.3 In-situ UV on Blanks and Pattern Mask

A mask blank (Ru/multilayer/quartz) was exposed for 12 hours under a low pressure IUV lamp. EUV reflectivity was measured before and after exposure. Figure 7 shows a comparison of the results achieved.

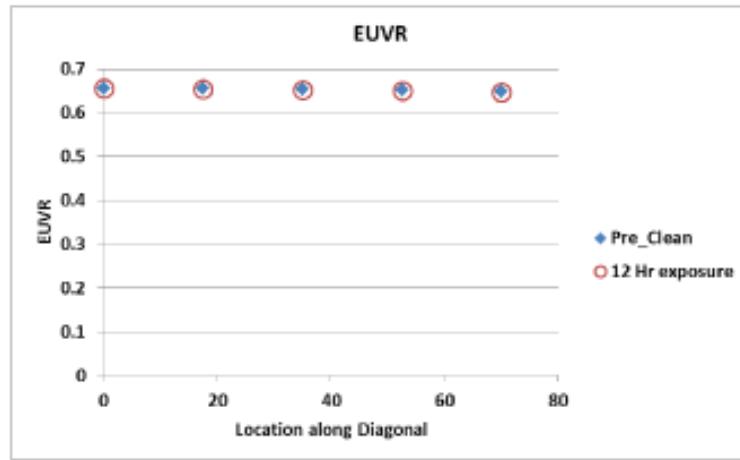


Figure 7. Reflectivity measurements at 13.5 nm (EUVR) measured before and after 12 hours of IUV irradiation with a low pressure lamp (corresponding to an exposure dose of approximately 100 x cleaning processes); no reflectivity loss was observed after this treatment.

The graph in Figure 7 shows that no damage, represented by reflectivity changes at 13.5 nm, was observed after IUV exposure of a EUV blank with a low pressure lamp. This result is in line with previous observation using the medium pressure lamp. Surface roughness was measured after treatment and a 0.136 nm roughness was observed.

A pattern mask was exposed in stationary mode to both medium pressure and low pressure lamps; SEM images were taken before and after exposure. Figure 8 shows the comparison of SEM images from the EUV mask surfaces after the different exposure scenarios.

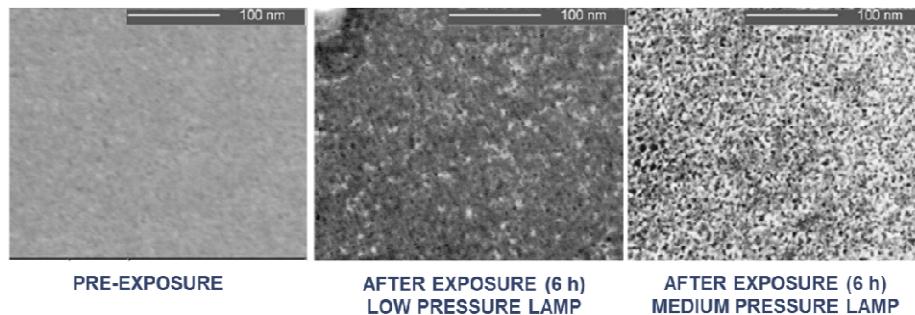


Figure 8. Pre-exposure (left) and post-exposure with low pressure (middle) and medium pressure (right) lamps. Severe damage is observed on the surface for medium pressure lamp exposure; impact is drastically reduced after exposure with a low pressure lamp.

Six hours exposure to a medium pressure lamp showed severe damage of the surface with pin-hole formation on the Ru layer; the impact of exposure is drastically reduced after an exposure with a low pressure lamp.

## 5 CONCLUSIONS

EUV masks are more likely to be cleaned than traditional 193 nm masks, due to the lack of a pellicle . Particle deposition and carbon contamination can occur at several points in time during the mask's lifetime, particularly during handling and exposure steps. In addition to these degrading effects, Ru damage is often observed in the form of volatile RuO<sub>4</sub> formation. In this paper possible root causes for the Ru damage have been presented. A two-fold mechanism has been proposed involving photochemical erosion and thermal stress. The manufacturing process of the mask itself seems to also play an important role, since specific damage behaviors are observed only for pattern masks and vary depending on the mask origin. A hardware solution for a cleaning tool feature is presented to overcome the photochemical erosion and thermal stress. A low pressure lamp experimental set-up has been described and experiments on pattern masks revealed significant improvement. Further studies were conducted to separate the photochemical and thermal contributions and to find the optimum process conditions to achieve a minimum of 100 cleans without critical impact to the functional layers of EUVL masks.

## ACKNOWLEDGEMENTS

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