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High aspect ratio titanium nitride trench structures as plasmonic biosensor

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Abstract: High aspect ratio titanium nitride (TiN) grating structures are fabricated by the combination of deep reactive ion etching (DRIE) and atomic layer deposition (ALD) techniques. TiN is deposited at 500 °C on a silicon trench template. Silicon between vertical TiN layers is selectively etched to fabricate the high aspect ratio TiN trenches with the pitch of 400 nm and height of around 2.7 μm. Dielectric functions of TiN films with different thicknesses of 18 - 105 nm and post-annealing temperatures of 700 - 900 °C are characterized by an ellipsometer. We found that the highest annealing temperature of 900 °C gives the most pronounced plasmonic behavior with the highest plasma frequency, \( \omega_p = 2.53 \text{ eV} \) (\( \lambda_p = 490 \text{ nm} \)). Such high aspect ratio trench structures function as a plasmonic grating sensor that supports the Rayleigh-Woods anomalies (RWAs), enabling the measurement of changes in the refractive index of the ambient medium in the wavelength range of 600 - 900 nm. We achieved the bulk refractive index sensitivity (BRIS) of approximately 430 nm/RIU relevant to biosensing liquids.

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1. Introduction

Plasmonics has been a constantly growing research area for the last two decades merging the fields of optics and nanophotonics where surface plasmons, collective oscillation of electron density, play a key role to confine light at nanoscale [1]. Various applications range from telecommunication [2,3] to solar energy harvesting [4,5]. Nevertheless, one of the most promising applications of plasmonics is sensing (biosensing) [6–16]. Such sensing devices have been developed utilizing plasmons properties to concentrate and enhance electric fields in very confined volumes close to the metal surfaces, thus tracing very small amounts of analytes in label-free biosensors, which may lead to point-of-care (POC) devices for swift, facile, and inexpensive diagnosis in future health care [17]. Plasmonic grating sensors and periodic structures made of plasmonic elements with a negative permittivity have been widely investigated for its potentiality of multiplexing of sensing units, achieving high throughput integration on lab-on-a-chip systems [12]. Sensing units typically require high robustness and stability, since, in many cases, they should sustain hours of continuous measurements. Traditionally applied plasmonic materials such as silver and gold are expensive and not compatible with CMOS processing. Moreover, silver suffers from oxidation and gold’s melting point do not allow it for refractory implementations.

Titanium nitride (TiN) is a highly-refractory material that exhibits plasmonic response in the visible and near-infrared (IR) wavelengths [18–29]. TiN is more abundant and cheaper than Au,
hard, stable, and biocompatible and has the high melting point. Another advantage of TiN over noble metals is the possibility of tuning the permittivity by varying deposition conditions and post-treatment. TiN films are deposited by reactive magnetron sputtering [20, 25, 29], nitridation of TiO₂ [26, 27], chemical vapour deposition [18] and the atomic layer deposition (ALD) technique [28, 30]. Especially ALD enables conformal deposition of plasmonic and dielectric layers with nanometer precision and as a consequence realization of large-scale dielectric multilayer [31, 32], dielectric trenches [33], plasmonic pillars [34–36] and trench metamaterial structures [37] with exceptional uniformity in large areas.

Here, we demonstrate surface sensitivity of high aspect ratio TiN trench structures towards the refractive indices of different ambient liquids for potential biosensing applications. The sensitivity of our sensing unit, 430 nm/RIU, originates from the Rayleigh-Woods anomalies (RWAs) on plasmonic grating, which changes the relevant reflection peaks with different refractive indices of surrounding media [8, 13, 14]. Our TiN-based trench structures were realized by the combination of ALD with advanced deep reactive ion etching (DRIE). The fabrication procedure is based on ALD deposition of TiN films on sacrificial Si templates with sub-sequential removal of Si. Optical characterization of flat TiN films with various thicknesses was conducted by an ellipsometer to show the thickness and annealing temperature dependences of the films parameters. TiN films exhibit a negative permittivity above the wavelength of 490 nm for annealing temperature of 900 °C. This article is organized as follows. In section 2, we describe the fabrication process of TiN films and trench structures. Section 3 deals with the characterization of sensing performance of the TiN grating structures, as well as the theory and numerical analysis on RWAs. Finally, we provide conclusion and outlook of TiN trench-based sensing devices and other applications.

2. Fabrication and characterization of TiN thin films

Prior to the grating fabrication, the growth conditions and the optical properties of flat TiN thin films were investigated. All fabrication procedures were carried out in a class 100 cleanroom.

2.1. ALD growth conditions

The deposition of TiN was performed in a commercial hot-wall reactor (R-200 Advanced Plasma ALD from Picosun) at 500 °C using TiCl₄ and NH₃ precursors. The growth rate was found to be 0.025 nm/cycle. 18 nm, 55 nm, 105 nm, 118 nm and 142 nm thick TiN films were deposited on double side polished Si substrates. The thicknesses were measured by spectroscopic ellipsometry and confirmed by SEM cross-sectional measurements. Table 1 summarizes the parameters of the ALD recipe used in this work.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Number of ALD cycles</th>
<th>Carrier gas flow (sccm)</th>
<th>Pulse time (s)</th>
<th>Purge (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiCl₄</td>
<td>950-4500</td>
<td>100</td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>NH₃</td>
<td>950-4500</td>
<td>100</td>
<td>2.0</td>
<td>6</td>
</tr>
</tbody>
</table>

Optical properties of TiN depend significantly on post-treatment. In this work, the dielectric function of TiN was evaluated as a function of the post annealing temperature.

2.2. Annealing

Annealing was performed in a conventional furnace (PEO-604 from ATV Technology). The process of annealing is illustrated in Fig. 1(a). The investigated temperature region was from 700 °C to 900 °C by the increment of 100 °C. The samples were placed in the furnace and several pump-purge steps were performed at the room temperature during one hour in order to minimized oxygen content in the chamber and consequential oxidation of the samples. Through the next
30 min, the temperature was raised to either 700 °C, 800 °C, or 900 °C and the samples were annealed for 1 hour in vacuum with N₂ flow of 20 sccm. After annealing the chamber was cooled down in vacuum with 5 sccm N₂ until the room temperature.

![Figure 1](image)

**Fig. 1.** Annealing of TiN samples 18 nm, 55 nm, 105 nm and 118 nm. (a) Annealing recipe. (b) Annealing result in terms of annealing temperature, plasma frequency (red), and imaginary part of permittivity at the plasma frequency (blue).

### 2.3. Optical properties of TiN films

The complex permittivity of TiN films were studied using spectroscopic ellipsometry (Ellipsometer VASE from J.A. Woolam Co.). This technique measures ellipsometric angles \( \Psi \) and \( \Delta \), which are the amplitude ratio and phase difference between p- and s- polarized light waves. For evaluation of the dielectric function of TiN, the Drude Lorentz oscillation model is conventionally applied [38].

\[
\varepsilon(\omega) = \varepsilon_{\infty} \left(1 - \frac{\omega_p^2}{\omega^2 + i\gamma}\right) + \sum_j \frac{S_j \omega_{f,j}^2}{\omega_{f,j}^2 - \omega^2 - i\Gamma_j}
\]  

(1)

In this equation, the Drude term describes free electrons and the Lorentz oscillators (the summation term in Eq. (1)) take interband transitions into account. The Drude term contains parameters, \( \varepsilon_{\infty} \), \( \omega_p \), and \( \gamma \), which are the high frequency dielectric constant, plasma frequency, and electrons plasma damping, respectively. The Lorentzian part of dielectric function \( \varepsilon(\omega) \) is characterized by \( S_j \), \( \omega_{f,j} \), and \( \Gamma_j \), which are the strength, resonance frequency and damping for the \( j^{th} \) Lorentz oscillator respectively. The results of fitted permittivity for all samples are shown in Fig. 2. The TiN permittivity depends on thickness as presented in Fig. 2(a). For films with thicknesses 118 nm and 142 nm (not shown here), the permittivity is not different from that of 105 nm, therefore they were excluded from presentation. Generally, the ALD deposited TiN has less metallic permittivity compared to sputtered films [24, 28], where \( \varepsilon_1 \) decreases more rapidly as the function of the wavelength. The main reason is the high oxygen content (up to 10 at. %) in ALD films. This can be improved by post annealing, which also leads to the blue shift of plasma frequencies of TiN. The same behavior was observed in all samples with all thicknesses as shown in Fig. 2(b)-(2d). The highest plasma frequency was observed for the thickest 105 nm samples. As-deposited TiN film has the plasma frequency of 1.86 eV (\( \lambda_p = 665 \) nm) and it increases to 2.53 eV (490 nm) upon annealing at 900 °C. The plasma frequency increases linearly with the annealing temperature, while the imaginary part of the permittivity at the plasma frequency decreases as displayed in Fig. 1(b). Similar behavior has been previously observed [24] for DC reactive sputtered films, where the annealing led to the increase of the material grain sizes and as
a result the decrease of the grain boundaries, improving free carrier density and blue-shift of plasma frequency.

2.4. Fabrication of TiN trench structures

Structured samples were fabricated by formation of a TiN-ALD deposited layer in a pre-defined, sacrificial Si template with subsequent removal of the Si host, leaving a negative replica of the template structure. As a result we have a functional TiN grating. The similar procedure was previously reported for other ALD deposited materials [33,37].

<table>
<thead>
<tr>
<th>Process parameters</th>
<th>TiN etch (1st ICP)</th>
<th>Si etch (2nd ICP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (℃)</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>Coil Power (W)</td>
<td>1200</td>
<td>400</td>
</tr>
<tr>
<td>Platen Power (W)</td>
<td>200</td>
<td>3</td>
</tr>
<tr>
<td>Time (s.)</td>
<td>180</td>
<td>285</td>
</tr>
<tr>
<td>SF₆ (sccm)</td>
<td>5</td>
<td>90</td>
</tr>
<tr>
<td>Ar (sccm)</td>
<td>5</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 3 illustrates the individual fabrication steps. The initial Si wafer (Fig. 3(a)) was selected, and grating pattern was defined by implementing deep-UV lithography (Fig 3(b)). Here, a 400 nm pitch was chosen for gratings and resist was exposed on area of 2×2 cm² (DUV stepper:
Fig. 3. Schematic of fabrication procedure. (a) Initial Si substrate. (b) Patterning of DUV resist. (c) Trench template fabrication using DRIE. (d) Conformal deposition of TiN inside Si trenches. (e) Etch of TiN using ICP. (f) Second ICP - etch of Si template, creating the TiN grating negative replica.

Canon FPA-3000 EX4). Next, deep-reactive ion etching (DRIE-Pegasus from SPTS) was used to create a sacrificial Si grating template (Fig. 3(c)) in a carefully optimized process reported elsewhere [37]. In the following step, the Si trenches were conformally coated with a TiN film by ALD (Fig. 3(d)) using the recipe described in Table 1. At this step prior to TiN grating formation in inductively coupled plasma (ICP) (Fig. 3(d)), the samples were annealed at 900 °C using previously mentioned procedure in order to improve plasmonic properties.

Fig. 4. Scanning electron microscopy images of the fabricated TiN trench structures. (a) cross section and (b) bird-eye-view (insets above and below show zoomed in image of the top part and the photo image of the actual sample, respectively).

The etch of TiN with both fluorine [39–41] and chlorine chemistries [42,43] in inductively
coupled plasma (ICP) systems has previously been reported. In this work, TiN top layer was removed in ICP (Multiplex ICP Etcher from SPTS) using the mixture of SF₆ and Ar. Subsequent Si template removal is also based on SF₆ isotropic etch. The etching parameters were selected in such a way that in the first case the top TiN layer is removed and the Si core becomes exposed, while in the second ICP run, Si needs to be removed without damaging the ALD deposited TiN replica structures. Etching parameters are presented in Table 2. A care needs to be taken in the last step (Fig. 3(f)) because Si etch between TiN replica is nonlinear in time and prolongation will lead to over-etch and possibly to collapse of the grating structures.

Each fabrication step was carefully evaluated by cross-section SEM (FE-SEM Supra 60VP from Zeiss). Figure 4 shows the final TiN grating structure in cross-sectional view (Fig. 4(a)) presenting the final grating height of $H = 2.7 \mu m$ with $\Lambda = 400$ nm pitch and bird-eye view image of the sample (Fig 4(b)). We will discuss the validity of the grating height later. The final high-quality structures have the aspect ratio of 1:6.8 and are on areas of $2 \times 2 \text{ cm}^2$ defined by the initial lithography step.

3. Refractive index sensing by TiN-based grating structures

![Fig. 5. TiN-based refractive index sensing system. (a) Schematic illustration of reflection measurement. The structure is assumed to be analyte layer on top of TiN/Air trench structures. (b) Simulated reflection of the trench structure of analyte-TiN/Analyte trench-TiN/Si trench-Si substrate structure with analyte of air (black), distilled water (DI, blue), ethanol (green), and isopropanol (IPA, red). The inset in (b) shows the norm of electric field of the trench structures at the wavelength of 707 nm when the analyte is air. Reflection from the grating structure in terms of wavelength and (c) thickness of TiN trench $t$ while keeping $\Lambda = 400$ nm, and (d) height of grating $H$ when $n_a = 1$ (air) and $\phi = 50^\circ$.](attachment:fig5.png)
Further, we demonstrate the capability of the fabricated TiN trench structures perform as grating sensors for refractive indices changes. We aim to characterize the sensitivity toward variations in the refractive index of the ambient medium. Typically periodic grating structures made of plasmonic components with a negative permittivity are used for biosensing [44–46] detecting the shift of the reflection peak in wavelengths (wavelength interrogation scheme) or change in the reflection angle (angular interrogation). Fig. 5(a) shows the geometry of reflection measurements. The structures are composed of Air-coverslip-analyte-TiN/Analyte trench-TiN/Si trench-Si substrate. TiN/Analyte and TiN/Si mean that there is either analyte or Si between TiN trenches. TiN/Analyte trench has the pitch of $\Lambda = 400$ nm, height of $H = 2.7$ µm, with the airgap of 200 nm, and thickness of TiN trench, $t = 200$ nm. TiN/Si trench has the height of $h = 0.2$ µm.

The BK-7 coverslip glass with thickness of 180 µm is placed above the TiN trench structures in order to contain the analyte liquid on TiN trench surface and to maintain the surface of liquid flat. It is known that regular gratings can show abrupt spectral changes in reflection, which are referred to as the Rayleigh-Woods anomalies (RWAs) [47,48]. They occur at the wavelength where different orders of transmission or reflections become tangential to the interface [47, 48]. The condition of RWAs are given by:

$$K_{\parallel} + mG = n_a \cdot K_0.$$  \hspace{1cm} (2)

Here, $K_{\parallel} = K_0 \sin \phi$ is the wave vector component parallel to the sample surface, $G$ is the grating vector equal to $2\pi/\Lambda$, $m$ is the order of the RWA and $n_a$ is the refractive index of the surrounding medium (analyte). Solving this equation gives the condition for RWA wavelength:

$$\lambda = \frac{\Lambda}{m} (n_a \pm \sin \phi),$$ \hspace{1cm} (3)

where $\phi$ is the angle of incidence in the analyte. For instance, when $n_a = 1$(air), $m = 1$, and $\phi = 50^\circ$, Eq. (3) gives $\lambda = 706$ nm.

In order to analyze the optical responses of the grating structure with different analyte liquids, we conducted numerical analysis based on the finite element method (COMSOL software package). Fig. 5(b) shows the simulated reflection from the TiN grating structures for air ($n_a = 1.000$), distilled water (DI, $n_a = 1.327$), ethanol ($n_a = 1.357$), and isopropanol (IPA, $n_a = 1.371$) for transverse magnetic (TM) incident light. Note that angle of incidence $\phi$ differs depending on the analytes’ refractive indices ($n_a$); $\phi = 50.0^\circ$ for air, $\phi = 35.3^\circ$ for distilled water, $\phi = 34.4^\circ$ for ethanol, $\phi = 34.0^\circ$ for isopropanol. In the simulation we assumed that the analyte liquids completely fill the trenches because the depth of liquid infiltration in the trenches does not significantly disturb the wavelength of the reflection peaks according to our COMSOL simulations (not shown here). Figure 5(c) shows the reflectance in terms of the wavelength and thickness of TiN trench, $t$, while the pitch is kept constant, $\Lambda = 400$ nm. We can see from the figure that trench thickness of $t > 200$ nm leads to broader reflection peak, which is detrimental for sensing. Therefore our 200 nm thick TiN trench width provides a sufficiently sharp reflection peak. From Fig. 5(d) for reflection in terms of the height of the trench, we can see that the width of reflection dip associated with RWA depends on the height of trench with its peak wavelength at 707 nm. For $H > 1.5$ µm, the reflection peak is not affected by the height while especially for $H < 1.0$ µm the shape of reflection peak strongly depends on the height. Therefore, the height of $H = 2.7$ µm in our current experimental setting is sufficient to avoid any deviation of the reflection peak associated with RWA.

We conducted free-space reflection measurements for the structure with TM-polarized light and incident angle $\phi_1 = 50^\circ$ as depicted in Fig. 5(a). The light source was a supercontinuum broadband laser (SuperK; NKT Photonics A/S, emission wavelength $\lambda = 350 - 2400$ nm) and we have an optical spectrum analyzer (OSA, Yokogawa Electric Corp. detection range $\lambda = 500 - 1750$ nm) as a detector of the reflected signal. The incident laser beam has a solid angle of $\pm 0.6^\circ$. 
Fig. 6. Measured reflection from the TiN trench structures for different analytes such as air, distilled water (blue), ethanol (green), and isopropanol (red) in the wavelength range of (a) $\lambda = 600 - 900$ nm and (b) 800 - 900 nm. Note that the dashed square in (a) corresponds to (b). Colored shade represents an error bar.

It is collimated, polarized by a film polarizer and focused at the sample interface via a set of parabolic mirrors. The specular reflected light was collected to a multimode fiber using another parabolic mirror and fed into the OSA. For reference the spectrum of the beam reflected at 50° incidence angle with an aluminum mirror is taken. Each analyte was measured 10 times to eliminate the fluctuation of the laser power and we took the average value of reflection. Note that the reflection measurements for three liquids were conducted with a short pass and long pass filters to eliminate incident light with the wavelengths below 800 nm and above 900 nm in order to avoid parasitic heating of the liquids, which can considerably change their refractive indices.

Table 3. Calculated and experimentally observed position of RWA peaks ($m=1$).

<table>
<thead>
<tr>
<th>Refractive index</th>
<th>Theory (nm)</th>
<th>COMSOL simulations (nm)</th>
<th>Experiment (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air ($n_a = 1$)</td>
<td>706</td>
<td>707</td>
<td>705</td>
</tr>
<tr>
<td>Water ($n_a = 1.327$)</td>
<td>837</td>
<td>838</td>
<td>834</td>
</tr>
<tr>
<td>Ethanol ($n_a = 1.357$)</td>
<td>849</td>
<td>850</td>
<td>847</td>
</tr>
<tr>
<td>Isopropanol ($n_a = 1.371$)</td>
<td>855</td>
<td>855</td>
<td>853</td>
</tr>
</tbody>
</table>

Figure 6(a) shows the measured reflection from the air-filled TiN grating structures with and without coverslip glass on top of the trench structure, and distilled water, ethanol, and isopropanol as different analytes between the coverslip glass and the trench structure. The refractive index range of water and isopropanol, $n_a = 1.327 - 1.371$, covers most of relevant refractive indices for biological sensing, such as urine $n = 1.337 - 1.348$ [49] or serum (blood) $n = 1.351 - 1.354$ [50]. When there is no analyte liquid (just air, $n_a = 1.000$), the reflectance peak is located at 705 nm as shown in Fig. 6(a). In the case of distilled water, the peak appears at 834 nm. For ethanol and isopropanol, the reflectance peak shifts to 847 nm and 853 nm, respectively. We observe a qualitatively good agreement between the simulation in Fig 5(b) and experimental results as in Fig. 6(b). The positions of RWAs peaks calculated using Eq. (3), simulated by COMSOL and experimentally observed are summarized in Table 3. The low reflection and shift of resonance peaks in experimental case from theory and simulated ones are due to the rough surface of the top part of the trenches as we can see from the scanning electron microscope pictures in the inset of Fig. 4(b). We also estimate that the slight difference of reflection peaks calculated by theory...
and COMSOL is due to the fact that COMSOL simulation dealt with trench structure with round corner on top (see the inset of Fig. 5(b)). Moreover, the variation of reflectance among different liquids can be caused by the uncertainty of liquid thickness between the trench structure and cover glass, and alignment of cover glass. The bulk refractive index sensitivity (BRIS) of sensors for wavelength interrogation is defined as the ratio between resonance shift $\Delta \lambda$ and refractive index variation of analyte, $\Delta n$, [15]

$$S_b = \frac{\Delta \lambda}{\Delta n} [nm/RIU], \tag{4}$$

where RIU stands for a refractive index unit. According to Eq. (4) overall bulk sensitivity between distilled water and isopropanol is $S_b = (853 \text{ nm} - 834 \text{ nm}) / (1.371 - 1.327) = 431 \text{ nm/RIU}$; between distilled water and ethanol, and ethanol and isopropanol, $S_b = (847 \text{ nm} - 847 \text{ nm}) / (1.371 - 1.357) = 429 \text{ nm/RIU}$, respectively. Hence, the TiN trench structure exhibits an averaged bulk sensitivity of approximately 430 nm/RIU. The measured $S_b = 430 \text{ nm/RIU}$ is comparable to the previously reported sensitivities for periodic metallic (plasmonic) nanostructures for biosensing with 300 - 600 nm/RIU in the visible to near infrared wavelength range including sensors based on the RWAs principle [12]. Reported sensitivities over 1000 nm/RIU were achieved for telecommunication wavelengths around $\lambda = 1500 \text{ nm}$ [14] with a larger grating period as the BRIS of RWAs-based sensors scales with their pitch [13]. Moreover, the sensitivity our structure is also comparable and even slightly outperforming those of all-dielectric structures in the near-infrared wavelengths, such as dielectric photonic crystal biosensing platform with 310 nm/RIU for HIV virus detection [44,45], Si resonators with 227 nm/RIU for cancer biomarker detection of prostate specific antigen (PSA, limit of detection, LOD: 0.87 ng/ml) [51], high-contrast grating resonator with 418 nm/RIU for label-free detection of cardiac disease biomaker, serum cardiac troponin I (LOD: 0.1 ng/ml) [46].

4. Summary and conclusion

In summary, we fabricated the high aspect ratio TiN trench structures by combination of DRIE and ALD. The fabricated structures are composed of 200 nm thick vertical TiN trenches with the height of 2.7 $\mu$m and pitch of 400 nm. The trench structures have dimensions of $2 \times 2 \text{ cm}^2$. These structural parameters can be controlled and optimized for various applications by the mask for deep-UV lithography and the subsequent processes, providing more flexibility in design of the trench structures and related metamaterial platforms with extreme anisotropy for steering of optical signals on the surface of metamaterials for longer wavelengths in the near-infrared and mid-infrared regions [37,52–60]. The deposited TiN films become plasmonic in the visible wavelength of around 490 nm (2.53 eV) for annealed ones at 900 °C as opposed to 665 nm (1.86 eV) of as-deposited films. Their optical properties also depend on the thickness of the TiN film, as well as the annealing temperature. Finally, the TiN trench structures are used as grating sensors based on the Rayleigh-Woods anomalies to measure the change in the refractive index of liquids whose refractive index is relevant for prospective biosensing applications. The achieved bulk refractive index sensitivity of 430 nm/RIU is close to or slightly outperforming similar plasmonic and dielectric grating sensors that can detect cardiac disease biomarkers, viruses, and cancer biomarkers. Our TiN-based structures can, in principle, be optimized in order to provide high sensitivity enabled by flexibility in various design parameters on-demand, such as, height, pitch, surface areas, and plasmonic properties of the trench by annealing, or depositing additional dielectric and plasmonic layers. Abundance of TiN, and the fabrication method well-suit for mass production of potentially cheap sensors. Therefore, such TiN-based sensors can be an attractive sensing platform at point-of-care diagnosis devices.
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