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# STM-Induced Luminescence for Alkanethiol Films on Au(111) Surface

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STM-induced luminescence spectra for organic molecule adsorbed Au(111) surfaces were studied, and the influence of STM-tip alloy material on the emission spectra was measured. We observed the STM-tip dependent emission spectra of Au(111). The characteristics of the spectra with Pt–Ir alloy(20%) tip are interpreted in terms of the one-mode type and two-mode type depending on the composition rates. We measured the emission spectra for two different types of molecules, decanethiol and octanedithiol, which have different adsorption structures. The emission spectra for the octanedithiol films were compared with the spectra from clean gold films and the decanethiol films. A spectral change of Au(111) due to adsorption of octanedithiol molecules on Au(111) was observed in the spectral range from 700 through 780 nm while not for the adsorption of decanethiol molecules. The spectral change due to adsorption of octanedithiol molecules is compared with the STS measurements.

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## 1. Introduction

Light emission induced by tunneling electrons from the STM junction is a feasible technique for the optical properties on a nanometer scale [1–9]. The tech-

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nique has been applied to the study of local electronic properties of metals and semiconductors. Recently, some experiments of STM-induced luminescence have been focused on the inorganic molecules on the metal surface as well as organic molecules [3–7], but the emission spectra have not been well understood. Further experiments of STM-induced luminescence for the adsorbed molecules for different types of molecules are needed to be correlated with the properties of adsorbed molecules. In this study, we have measured the luminescence for the inorganic molecules on metals, i.e. self-assembled monolayers (SAMs), with different adsorption structures.

Self-assembled monolayers have attracted considerable interest in the field of thin films on solid because of their highly ordered structure [10–18]. In particular, the structure of alkanethiol ($CH_3-(CH_2)_{n-1}-SH$) SAMs on Au(111) surface has been intensively studied by STM and atomic force microscopy (AFM). This molecule has one thiol-group, S–H, and the molecules are in a standing position at the angle of about 50 degree with respect to the surface normal with covalent bonding of sulfur to the gold atom. On the other hand, alkanedithiol molecules $HS(CH_2)_nSH$, which have two thiol-groups, are adsorbed in parallel to the surface with two S–Au bondings.

In this study, the alkanedithiol (having two thiol-groups) films on Au(111) have been studied by means of STM-induced luminescence, and recorded the spatially and spectrally resolved photon map. The spatially averaged emission spectra for the octanedithiol films have been compared with the spectra from clean gold films and the decanethiol films.

For the spectral study of STM-induced luminescence, it is important to consider the effect of STM tip on the emission spectra because the STM-induced emission spectra depend on the material of STM tip as well as the sample itself. In the experiment, we often use a tip material which is stable at high bias voltages, and produces a high intensity of light. In this sense, Pt–Ir alloy is often used for the STM-induced light measurements. In this paper, we have studied the STM-induced emission spectra of Pt–Ir alloy by measuring the emission spectra for the system of Au(111) surface and Pt–Ir STM tips. Pure Pt and two different Pt–Ir alloy tips have been used. We have observed the STM-tip dependent emission spectra. The emission spectra with Pt–Ir(20%) tip are not well reproduced, being very sensitive to the nature of the tip apex, while the spectra with pure Pt or Pt–Ir(10%) tips are reproducibly obtained.

In the STM-induced luminescence of organic molecules on Au(111), we have observed a spectral change due to adsorption of octanedithiol molecules on Au(111) in the spectral range from 700 through 780 nm while not for the adsorption of decanethiol molecules. The spectral change due to adsorption of octanedithiol molecules is discussed in relation to the adsorption structure, and bonding nature of S–Au and alkyl chain with Au(111).

## 2. Experimental setup

The spectra mapping measurements of STM-induced luminescence have been made simultaneously with STM images by using an in-house made UHV-STM combined with the photon detection system [8, 9]. Photons emitted from the tip–sample junction are collected using an ellipsoidal mirror. Then the light focused by the mirror is guided to a spectrograph through optical fibers. The spectra are recorded with ICCD detector (ICCD-1024E, Princeton Instruments, Inc.). By acquiring emission spectra while scanning the tip position, a constant current topographic image and spatially resolved emission spectra can be simultaneously obtained. A spectrum is integrated for around 1.0 s at each point of $64 \times 64$ points in the scan region. The spectra are recorded at the sample bias of 2.0–2.5 V and the tunnel current of 0.5–4.0 nA.

The spectral sensitivity of the optical system used in the present experiments was measured to compare the experimentally observed spectra with theoretically calculated spectra. The theoretical spectra presented in this paper are considered with the optical sensitivity of the apparatus used.

The samples of alkanedithiol films are prepared by liquid reaction of decanethiol liquid (0.5 mM) or 1,8-octanedithiol liquid (5 mM) with the atomically flat Au(111) surface. After the liquid reaction, the sample is dried and annealed in air at about 70°C.

The tunneling tips used in the experiments are made by electrochemically etching tungsten (W), platinum (Pt), Pt–Ir(20%), and Pt–Ir(10%) wires.

## 3. Results and discussion

### *3.1. Effects of Pt–Ir alloy on the spectra*

The STM-induced light has been recorded for the atomically flat Au(111) surface with different tips of different material and compositions to observe the effect of STM tip material on the emission spectra. The emission spectra for different STM tips have been obtained from the data recorded by spatially resolved spectra.

The emission spectra with the use of W, pure Pt, or Pt–Ir(10%) tips were well reproducibly obtained, showing each characteristic spectral shape. On the other hand, the spectra with Pt–Ir(20%) alloy tips were not well reproduced experimentally, but different spectral shapes were frequently observed for different tips made from Pt–Ir(20%) alloy wire. Figure 1 shows examples of different spectra observed with different Pt–Ir(20%) tips. The sample of Au(111) has the atomically flat surface. Then, the different spectral change in Fig. 1 should be caused by the change of the tip property of Pt–Ir(20%) alloy. In these spectra, we can identify some spectral peaks around 640, 680, 700, 760 nm in wavelength. These different peaks cannot be expected for pure metals of W, Pt, Au, and were not observed

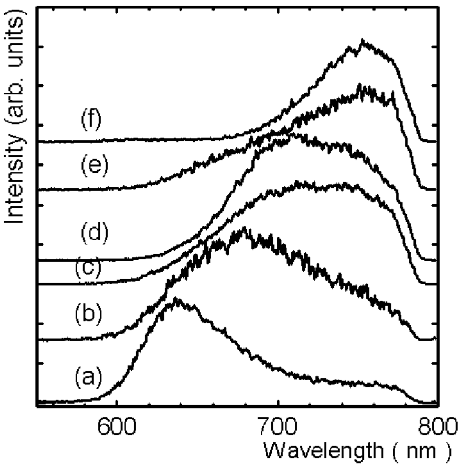

Fig. 1. Variations of STM-induced emission spectra for Au(111) surface observed with the use of different STM tips of Pt–Ir(20%).

experimentally for tips of W, Pt, Au, and Pt–Ir(10%). Therefore, this result can be attributed to the effect of alloying of Pt and Ir.

The spatial fluctuation of alloy composition may be significant on the scale of STM tip size in the range from about 50 through 200 nm where the local plasmon for the STM-induced luminescence is produced. The composition of Ir in Pt–Ir(20%) may have an important role in determining the geometric and electronic structure at the apex of STM tip. Therefore, the emission spectra from Au(111) surface for Pt–Ir tips with different compositions were calculated to explain the experimental results of different spectra shapes in terms of the spectra for the alloy materials with different compositions. The calculation is based on an electromagnetic theory with the complex dielectric functions for the materials of Au sample and STM tips [19–22]. In this theory, the tip is assumed as a metal sphere with a radius of the tip curvature radius, and the sample has a flat surface. The optical sensitivity of the optical system used is included in the calculation of spectra presented in this paper.

The electromagnetic properties of the tip and sample are described by the complex dielectric functions, $\varepsilon = \varepsilon(\omega)$ in this theory. The alloying of the materials is also expressed with the dielectric function of the alloy, $\varepsilon_{\mathrm{Pt-Ir}}$, by defining it with two dielectric functions, $\varepsilon_{\mathrm{Pt}}$ and $\varepsilon_{\mathrm{Ir}}$, of each component of the alloy, Pt–Ir. In the present calculation, the dielectric functions of the alloy, Pt–Ir, are defined in two different ways under the weight of the composition rate, $a$ and $b$ for Pt and Ir, respectively. The first definition is described in the following way:

$$\varepsilon_{\mathrm{Pt-Ir}} \equiv a\varepsilon_{\mathrm{Pt}} + b\varepsilon_{\mathrm{Ir}}. \tag{1}$$

Here, the new dielectric properties of alloy are produced in an intermediate way as the mixture of each component. The second definition may be given as

$$\frac{1}{\varepsilon_{\mathrm{Pt-Ir}}} \equiv \frac{a}{\varepsilon_{\mathrm{Pt}}} + \frac{b}{\varepsilon_{\mathrm{Ir}}}. \tag{2}$$

In this definition, the dielectric response of each component is assumed to be inversely proportional to respective $\varepsilon$ and each component of alloy responds independently to the electromagnetic sources under the weight of the composition rate. The results of the calculation are shown in Fig. 2 for different definition of $\varepsilon$ and different composition of the alloy. The experimental spectra are also shown in Fig. 2. In these calculations, the bias voltage is 2.06 V and the radius of STM tip is assumed to be 50 nm. The dielectric constants as a function of energy for Pt and Ir are used from the published data [23]. Figure 2a corresponds to the case of Eq. (2), and Fig. 2b to the case of Eq. (1). The spectra in Fig. 2a seem to be a superposition of two different modes at the peak position of around 620 and 760 nm in wavelength. On the other hand, the spectra in Fig. 2b exhibit a nearly single and broad peak. This kind of behavior of the spectra has been known as two-mode type (behavior) and the single-mode type (behavior) in the electronic and vibrational modes of mixed crystals [24]. In the present results, the observed spectrum (curve *a*) in Fig. 1 exhibits a similar spectral shape to the calculated spectrum *a* in Fig. 2a, and the observed spectra (curves *e* and *f*) in Fig. 1 represent a mode appearing around 760 nm in the calculated spectra in Fig. 2a. On the other hand, the observed spectra (curves *b*, *c*, *d*) in Fig. 1 show a similar spectral shape and the wavelength of the peak to the calculated spectra in Fig. 2b. The observed features for Pt–Ir(20%) in Fig. 1 may be interpreted by one type of two behaviors depending on the local tip properties. Which mode is a main contribu-

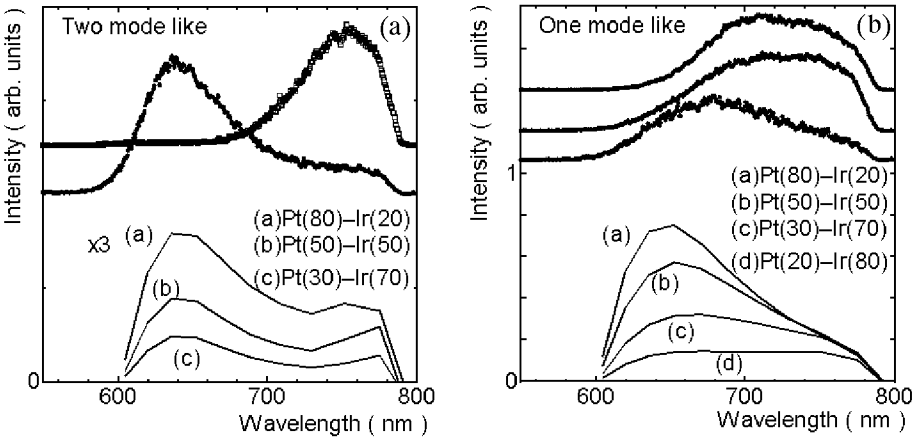

Fig. 2. The theoretical calculation of the STM-induced emission spectra with different Pt–Ir of different composition rates. The STM bias is 2.06 V and the radius of the tip is assumed as 50 nm. The dielectric functions used for the calculation are defined in two different ways as Eqs. (1) and (2). Part (a) is corresponding to Eq. (2) and part (b) to Eq. (1). The experimental spectra are also shown for comparison.

tion to the spectra may be dependent on the mixing condition of Ir in Pt at the apex of the Pt–Ir(20%) STM tip. If the phase of each component is rather spatially separated, the emission spectra should be explained by two-mode behavior, and if each component is well mixed uniformly, the spectra should be explained by one-mode behavior. Therefore, the variety of the observed spectral shape for Pt–Ir(20%) alloy is considered to represent a characteristic way of alloying on a local scale of the STM tip apex.

The Pt–Ir wires have been often used for the STM measurements. They are stable and suited for the topographic measurements, but the present experiments indicate that the Pt–Ir with a high concentration of Ir is not suited for the STM-induced luminescence because the observed spectra depend on the local tip properties. Therefore, the Pt–Ir(20%) tips have not been used in the experiments of the next section.

### *3.2. Spectral change of emission spectra due to molecule adsorption on Au(111)*

We have measured STM-induced luminescence for two different molecules, 1-decanethiol and 1,8-octanedithiol adsorbed Au(111) surface. The results for decanethiol films have been already reported elsewhere by the present authors [7]. They are summarized as follows, for the comparison with the present result: (1) The photon map, i.e. the map of the photon intensity, shows a contrast of etch pits which are produced during the film formation, which is well correlated with the topographic image (Fig. 3a). The scan area is 65.6 × 65.6 nm$^2$. (2) The shape of STM-induced spectra for the etch pit region is nearly identical to that of the outermost layer of the sample. (3) The emission spectra of molecule adsorbed Au(111) do not change their shapes due to the molecule adsorption from those of clean gold when we measure them in the range of bias voltage from 2.0 to 2.5 V (Fig. 3b).

Figure 4 shows an STM image of 1,8-octanedithiol film with etch pits which are a characteristic feature of alkanethiol films on Au(111). The etch pit is seen as a dark region (with low intensity), and the molecular arrangement with a shape like a cigar can be imaged in the figure.

Figure 5 shows the results of STM-induced luminescence. Figure 5a is a topographic image of the molecule-adsorbed sample and Fig. 5b is its photon map for the corresponding area measured at the same time as the topographic measurements with a bias voltage of 2.0 V and a tunneling current of 1.0 nA. The tip used is a Pt–Ir(10%) tip, and the scan area is 100 × 100 nm$^2$. The photon intensities of the photon map in Fig. 5b are obtained by integrating the intensity of spectra over a wavelength range from 400 through 800 nm at each of $64 \times 64$ points. The topographic image of SAM structure could not be well recorded at the same time of spectral mapping, while some etch pits were slightly seen

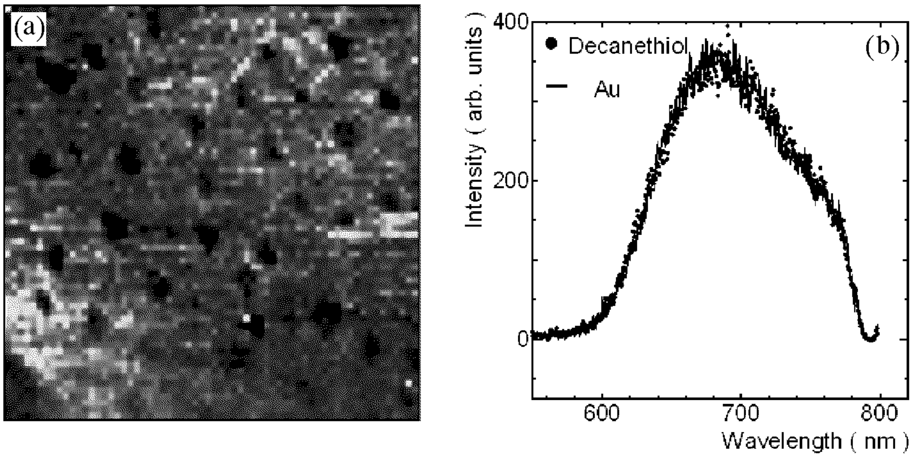

Fig. 3. (a) Photon intensity map of STM-induced light for the decanethiol film on Au(111) surface. (b) Comparison of the emission spectra for octanedithiol adsorbed Au(111) (dot) and Au(111) without adsorption (line).

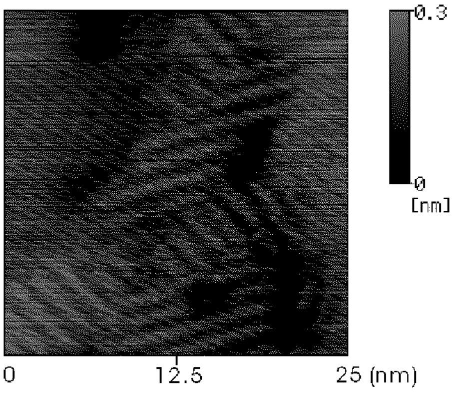

Fig. 4. STM images of the octanedithiol films on Au(111) surface.

around the bottom of the image. This is due to the fact that the measurement of STM image is generally unstable at the measurements during spectral mapping.

In Fig. 6, the emission spectra from the octanedithiol-adsorbed Au, curve 3, is compared with those from the decanethiol-adsorbed Au, curve 2, and from clean gold film, curve 1, with the use of Pt–Ir(10%) tip. We can see a spectral change due to adsorption of octanedithiol molecules on Au(111) in the spectral range from 700 through 780 nm. This spectral change can be reproduced for different Pt–Ir(10%) and W tips, then the effect of tip on the spectral change can be excluded.

We have observed a spectral change due to adsorption of octanedithiol molecules on Au(111) in the spectral range from 700 through 780 nm while not for the adsorption of decanethiol molecules. Here, we consider the reason for the

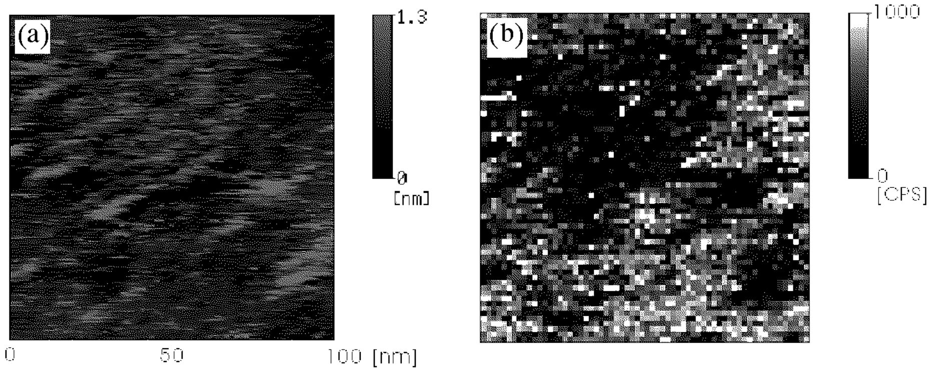

Fig. 5. (a) STM image of octanedithiol film on Au(111), and (b) photon map of STM-induced light measured at the same time as STM image (a).

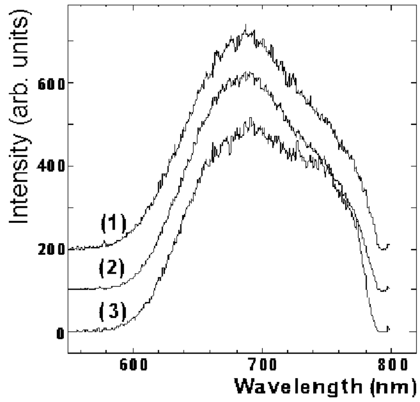

Fig. 6. STM-induced luminescence spectra for Au(111) (curve 1), decanethiol on Au(111) (curve 2), and octanedithiol on Au(111) (curve 3).

spectral change due to adsorption of octanedithiol molecules. The STM-induced photon emission spectra of the sample should be mainly caused by the local plasmon induced radiation from gold. If we could observe the spectral change due to adsorption on gold, we would consider the following mechanisms: (a) the effect of dielectric media (decanethiol molecules) which induces the change of plasmon modes due to the change of the boundary condition at the interface between gold and molecule layers, (b) the luminescence from the adsorbed molecules itself, (c) the change in the density of states of the metal sample due to the adsorption of molecules.

On the basis of the calculation of STM-induced light for the multilayer system which consists of gold film and a dielectric layer, the effect of a dielectric layer on the plasmon mode is negligibly small because of thin layer of molecules on gold. The luminescence from organic molecules could not be observed for the decanethiol molecules on Au(111). In this sense, the spectral change for octanedithiol molecules cannot be ascribed to the luminescence from molecules. On the third point (c), if there is a significant change in the density of states due to adsorption, the light emission spectra would change its shape from those of clean surface, depending on the density of states, because the local plasmon is excited by tunneling electrons through the states. The present results indicate the change of the spectra around 720–780 nm in wavelength (corresponding to the energy of 1.59–1.72 eV). This change would correspond to the change of the density of states above 0.4 eV (= 2.0–1.59) referenced to the Fermi level for the bias voltage of 2.0 V.

The STS measurements can be correlated with the local electronic structure of the surface probed by STM tip. Thus, the current vs. bias voltages were measured for the octanethiol adsorbed Au(111) surface. The derivative of the current with bias voltage, $\mathrm{d}I/\mathrm{d}V$, is plotted in Fig. 7a (filled circles), and compared with the emission spectra (Fig. 7b). The data of $\mathrm{d}I/\mathrm{d}V$ for pure gold surface are also plotted in the figures (open circles). Figure 7b shows a comparison of the emission spectra between octanedithiol adsorbed Au and clean Au film. The difference spectrum is also plotted. The result of $\mathrm{d}I/\mathrm{d}V$ for octanedithiol indicates the increase in the derivative around 0.5 V and decrease around 0.8 V with respect to the result for gold. These values nearly correspond to the energy mentioned above from the experimental results of emission spectra.

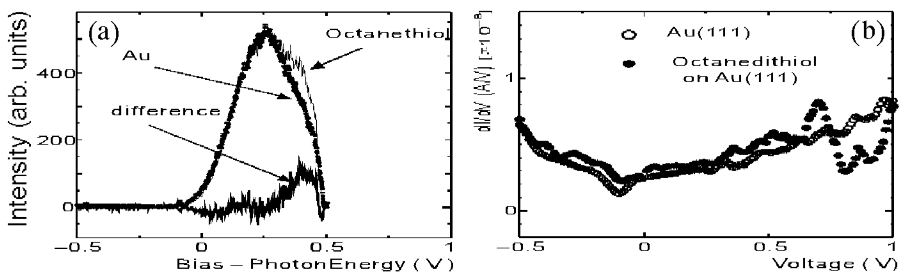

Fig. 7. (a) $\mathrm{d}I/\mathrm{d}V$ curve obtained from the data of current vs. bias voltage for Au(111) and octanedithiol adsorbed Au(111). (b) Comparison of emission spectra between curve 1 and 3 in Fig. 6.

The origin of the density of states around 0.5–1 eV observed for the octanedithiol film is not clarified in the present study, but may be identified with molecular orbital calculations of the adsorbed system. At present stage, on the basis of the experimental results that the spectra change was observed for octanedithiol molecules, and not for decanethiol molecules, the following fact should be noted in relation to the different adsorption geometry, i.e. standing molecular chain for decanethiol molecules and lying chain on Au surface for octanethiol: one possible effect is the change of electronic states in octanedithiol due to two S–Au bondings instead of one S–Au bond for decanethiol molecules, and another is the interaction of alkyl chain with Au surface. These facts should be related to the different electronic states. The calculation of molecular states on Au(111) is in progress.

## 4. Summary

We have studied the STM-tip dependent emission spectra for the Au(111) surface and the STM-induced luminescence from organic molecules adsorbed Au(111). The emission spectra with Pt–Ir(20%) tip are very sensitive to the nature of the tip apex while the emission spectra with the use of pure Pt or Pt–Ir(10%) tips are well reproduced. The STM-induced emission spectra for different STM tips have been calculated by the electromagnetic theory with complex dielectric functions defined in two different ways for alloy material, and have been interpreted in terms of the one-mode type and two-mode type depending on the composition rates. We have made the spectral mapping measurements of STM-induced luminescence for the octanedithiol molecules adsorbed on Au(111) surface. We have observed the spectral change due to adsorption in the spectral change from 700 to 800 nm in wavelength. The spectra were compared with the results of STS measurements, indicating the change of $\mathrm{d}I/\mathrm{d}V$ around 0.5–1.0 eV. This change in the density of states observed in $\mathrm{d}I/\mathrm{d}V$ is consistent with the observed spectra in STM-induced spectra for octanedithiol films.

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