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Metal-Insulator Transition Property of Hf-Doped VO_2 (M1) Films and Its Application for Reconfigurable Silicon Photonic Device

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Abstract—In this work, we report a novel phase change material: Hf-doped VO_2(M1) with negligible thermal hysteresis width for low-power silicon photonic reconfigurable device applications. As dopant concentration rises from 0% to 3%, the material maintains the metal-insulator transition (MIT) property of VO_2(M1) thin films, and the thermal hysteresis width significantly narrows from 7°C to < 1°C, leading to a good control of material electrical and optical constants as a function of temperature. A ring resonator with Hf-doped VO_2(M1) material partly deposited on the ring has been fabricated. Temperature dependent transmission spectrum of the device has been tested, which shows resonant peak shift due to the phase transition of Hf doped VO_2(M1). Doping Hf makes this material become a promising candidate for a variety of silicon integrated reconfigurable photonic devices.

1. INTRODUCTION

Monoclinic vanadium dioxide VO_2(M1) thin films featuring a metal-insulator phase transition (MIT) at 68°C is a promising candidate for silicon photonic modulator and optical switch applications [1, 2]. Due to the low phase transition temperature, a very low power density is required (10^{-11} J/μm^2 to 10^{-12} J/μm^2) for switching VO_2(M1) from the semiconductor to metal state. However, large thermal hysteresis is observed in the phase transition process of VO_2(M1). The different optical constants of VO_2(M1) at the same temperature during increasing or decreasing temperature ramps prevent one to access the intermediate phase states of VO_2(M1), and consequently limit the device applications only to binary phase states of VO_2(M1) (pure metal and pure insulator). Therefore, reducing the hysteresis of VO_2(M1) phase transition is very important for practical device applications. Some previous reports show that by using transition metal doping in vanadium oxides, such as Ti doped VO_2 and Mo doped VO_2 [3, 4], it is possible to reduce the thermal hysteresis during phase transition. However, a systematic study on the material's optical property during the phase transition process and its application to silicon photonic devices are not reported. In this study, we report Hf doped VO_2(M1) thin films with narrow thermal hysteresis for integrated reconfigurable silicon photonic device applications. It is observed that the optical properties of VO_2(M1) show significantly reduced hysteresis as a function of temperature. Finally, we prepared silicon ring resonators considering its importance for reconfigurable photonic devices application [5, 6]. Such properties lead to well controlled resonant frequency of a Hf:VO_2(M1) loaded silicon ring resonators as a function of temperature at telecommunication wavelengths.

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2. EXPERIMENTAL DETAILS

VO_2 thin films were deposited on SiO_2 substrates by pulsed laser deposition (PLD). A Compex Pro 205 KrF excimer laser operating at 248 nm wavelength was used for the deposition process. The substrates were firstly cleaned by acetone, isopropanol and de-ionized water with ultrasonication. Before thin film deposition, the base pressure of the PLD chamber was pumped to 5×10^{-6} Pa. A metallic vanadium target (Alfa Aesa, 99.99%) and a HfO_2 target (Alfa Aesa, 99.99%) were used for thin film fabrication. The different doping concentrations of Hf were achieved by alternatively ablating the V and HfO_2 targets with different number of laser pulses. The oxygen partial pressure was kept at 0.67 Pa during the deposition process, whereas the substrate temperature was kept at room temperature. The laser fluence was maintained to be around 1 J/cm^2. The deposition rate of Hf:VO_x thin films was 4.2 nm/min for a target to substrate distance of 5.5 cm and laser repetition rate of 10 Hz. After deposition, the films were transferred to a chamber with radiative heaters, and annealed at 500°C for 1 hour with oxygen partial pressure of 150 Pa to form vanadium oxide thin films. Five Hf:VO_2 thin films with Hf atomic concentrations of 0%, 1%, 3%, 5% and 8% were deposited as confirmed by energy dispersive spectroscopy (EDS) characterizations.

Phase identification of the Hf-doped VO_2 thin films was carried out by X-ray diffraction (XRD) on a Shimazu XRD-7000 X-ray diffractometer with Cu K_α radiation ($\lambda = 0.1542$ nm). All film thicknesses were measured to be around 50 nm on a JEOL7600F field emission scanning electron microscope (SEM). A four point probe measurement system equipped with a heater stage was used to characterize the film surface resistivity. Optical constants of all films at the semiconductor and metallic states were characterized by spectroscopic ellipsometry (RC2, J. A. Woollam). Confocal Raman microscopy study of the phase transition process was measured on a Reinishaw Invia Reflex Raman microscope. A

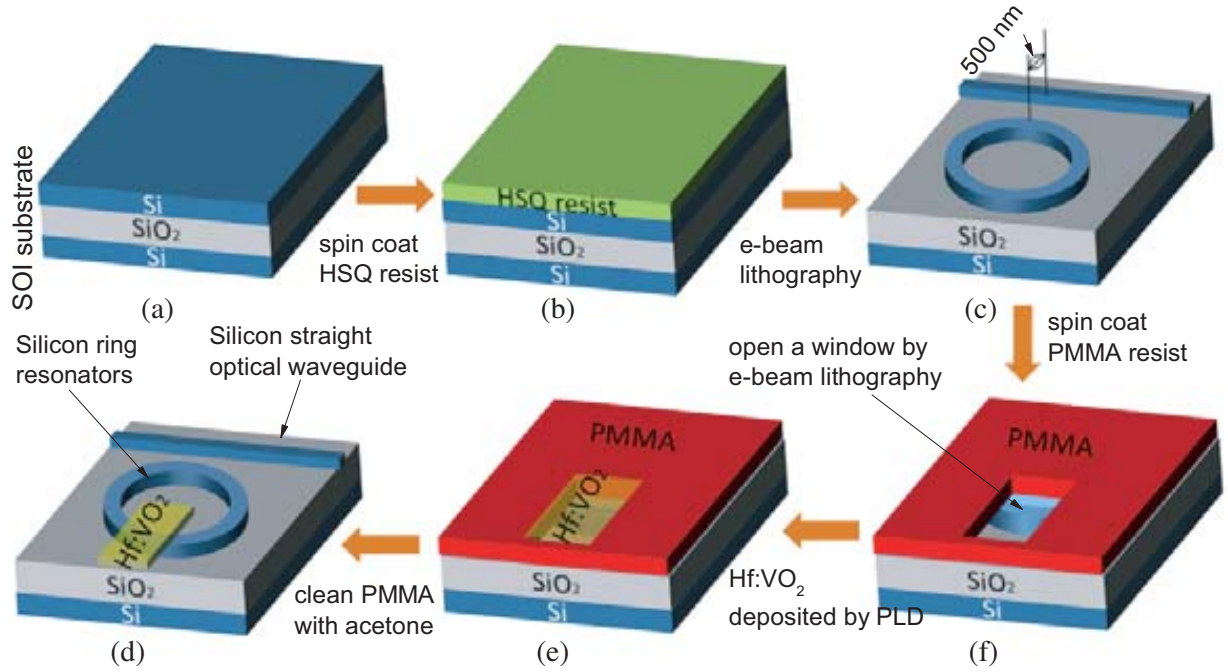

Figure 1. The schematic preparation process of the ring resonator devices. (a) Si/SiO_2/Si (Silicon-On-Insulator, SOI) substrate was coated with (b) hydrogen silsesquioxane (HSQ) resist. Then, (c) the silicon ring and silicon straight waveguide, with a distance of 500 nm, were prepared by e-beam lithography. Next, (d) spin coat the polymethyl methacrylate (PMMA) resist and then open a window by e-beam lithography. (e) After depositing the 3% Hf-doped VO_2 (Hf:VO_2) by PLD, the PMMA resist was cleaned using acetone to complete the (f) Silicon ring with depositing Hf:VO_2 on surface. Finally, the device was annealed at temperature 500°C in oxygen ambient for one hour to make Hf:VO_2 crystallization.

continuous wave laser operating at 514 nm wavelength was used for Raman spectrum study. Silicon ring resonator was fabricated by e-beam lithography with ring diameter of 20 µm. For the device, as shown in Fig. 1, 1 µm length of the ring resonator was covered with 3% Hf-doped VO_2 (Hf:VO_2, $\sim$ 50 nm thickness). The device was fabricated by depositing the Hf:VO_2 thin films on PMMA partially covered ring resonator, then lifted-off in acetone and annealed in oxygen ambient. The final device was characterized on a fiber end-coupled waveguide testing station equipped with a temperature stage.

3. RESULTS AND DISCUSSION

Figure 2(a) shows the XRD spectra of vanadium dioxide thin films with different Hf-doping concentrations. When Hf concentration is below 3%, the Hf:VO_2 thin film shows only diffraction peak at (011) plane of the monoclinic (M1) phase. The peak intensity decreases gradually, indicating the weaker M1 phase. With increasing Hf concentration to 5%, the (110) plane diffraction of VO_2(M1) phase appears, and the intensity of the (011) diffraction peak of monoclinic VO_2(M1) phase becomes weaker. Meanwhile, the secondary phase from VO_2 (B) appears, which shows several diffraction peaks at (001), (002), (003) and (−511) planes, suggesting the appropriate Hf concentration is less than 5% for preparing the Hf:VO_2(M1) thin films in our fabrication conditions. Further increasing the Hf concentration up to 8% leads to a phase transition to the single VO_2(B) phase [7]. Raman spectra of all Hf-doped VO_2(M1) thin films are shown in Fig. 2(b). Characteristic Raman peaks at $\sim$ 193 cm^{-1}, $\sim$ 223 cm^{-1} and $\sim$ 619 cm^{-1} from the VO_2(M1) phase are observed for all films with Hf concentration up to 3%, and these peaks' intensity declines obviously revealing the weakened VO_2(M1) phase, which is in agreement with the results of XRD patterns.

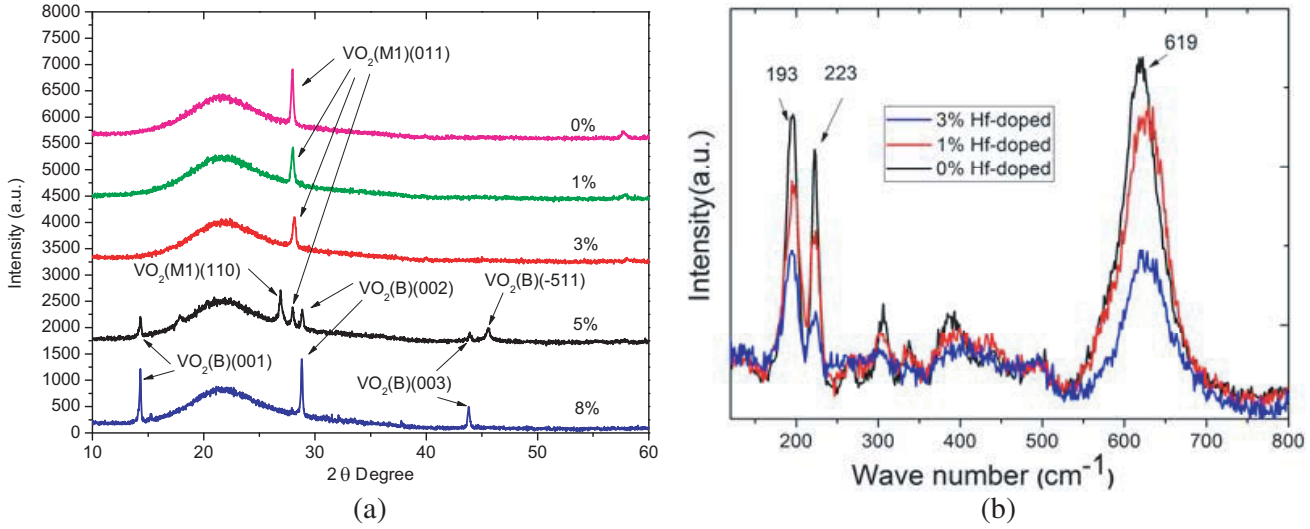

Figure 2. (a) XRD spectra of different concentrations of Hf-doped Vanadium dioxide films. (b) Raman spectra of different concentrations of Hf-doped Vanadium oxide films.

The phase transition of Hf doped VO_2(M1) thin films as a function of temperature is studied by sheet resistance and optical transmission characterizations as shown in Fig. 3. Electrical-resistivity versus temperature curves are shown in Fig. 3(a). About 3 orders of resistivity change and a clear hysteresis (width $\sim$ 7°C) during phase transition are observed in the pristine VO_2(M1) film, and the metal-insulator transition (MIT) temperature (T_{MIT}) for the pristine VO_2(M1) film is around $\sim$ 65°C, which is close to the bulk VO_2 T_{MIT} of 68°C. On the other hand, a significant decrease in resistance value at low temperature is observed in Hf-doped VO_2(M1) thin films (1% and 3%), which is possibly assigned to more impurity defects, and resulting in about 2 orders of magnitude resistivity change, whereas negligible hysteresis is observed in these samples, illustrating that doping Hf can effectively reduce the hysteresis width of VO_2(M1) thin films. With further increasing the Hf concentration up

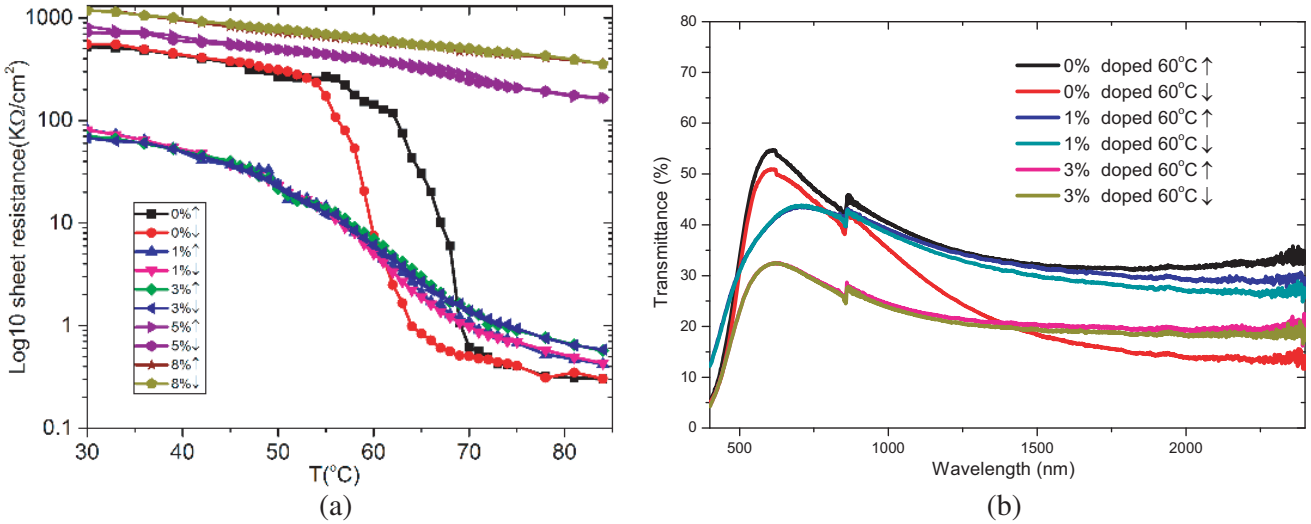

Figure 3. (a) Temperature dependent sheet resistance of the Hf:VO_2 thin films during heating and cooling processes; (b) Comparison of the transmittance spectrum of pure VO_2 and Hf-doped VO_2 thin films at 60°C during heating and cooling processes respectively.

to 5–8%, the VO_2(B) thin films shows no MIT property, consistent with the previous reports [8]. The optical transmittance of 0–3% Hf doped VO_2 is measured from 400 nm to 2400 nm wavelength range at 65°C during the heating and cooling cycles respectively (Fig. 3(b)). We noticed clear contrast of the optical transmittance, especially in the near infrared wavelength range for the pure VO_2(M1) sample corresponding to its hysteretic MIT process. For Hf-doped VO_2(M1) films, the optical transmittance is almost identical at 65°C during the heating and cooling cycles, with only slight difference in the near infrared wavelengths, due to the tiny hysteresis width.

The optical constants involving index of refraction and extinction coefficient for Hf:VO_2(M1) thin films at the semiconductor and metallic states are shown in Fig. 4. Clearly, all films show large optical constant variations due to the MIT process. Notice that the index of refraction is lower with increasing

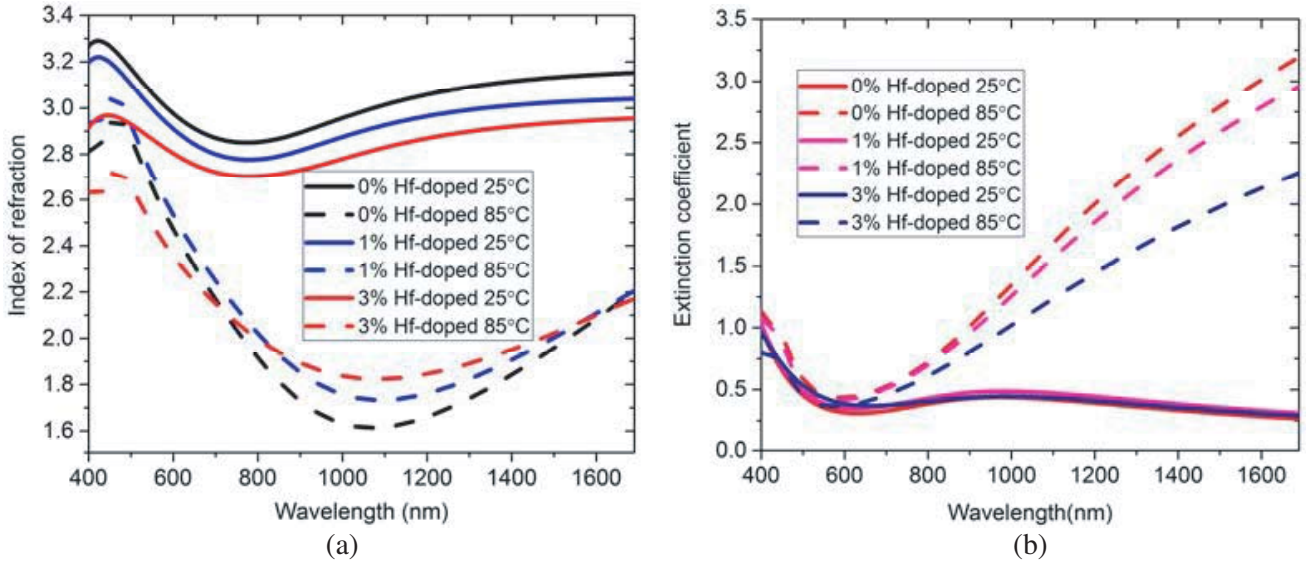

Figure 4. (a) Refractive index and (b) extinction ratio of different concentrations of Hf doped VO_2 thin films at 25°C and 85°C.

Hf concentrations, whereas the amplitude of phase transition induced optical constant change is also lower with higher Hf concentration (Fig. 4(a)). For the extinction ratio, three samples show very similar extinction ratio at their semiconductor states, whereas higher optical extinction ratio is observed with less Hf doping concentrations (Fig. 4(b)), which leads to wider modulation range for the pure VO_2(M1) thin film.

Figure 5 shows the SEM image of 3% Hf doped VO_2(M1) coated silicon ring resonator. In order to test the phase change effects of Hf:VO_2 on a silicon ring resonator, we firstly tested the transmittance spectrum of a pure silicon ring at 15°C and 80°C respectively, and the changes of the Q factor were too small to be measured (the related data was not presented in this paper). Next, we measured the transmittance spectrum of the device at 15°C and 80°C respectively to evaluate the effect before and after phase transition of Hf:VO_2(M1) on the resonance wavelength, as shown in Fig. 6. The broadening of the resonance wavelength is mainly due to the MIT process in Hf:VO_2(M1), proving the Hf:VO_2(M1) coated silicon ring resonator is reconfigurable. The resonance peak broadens at high temperature, with

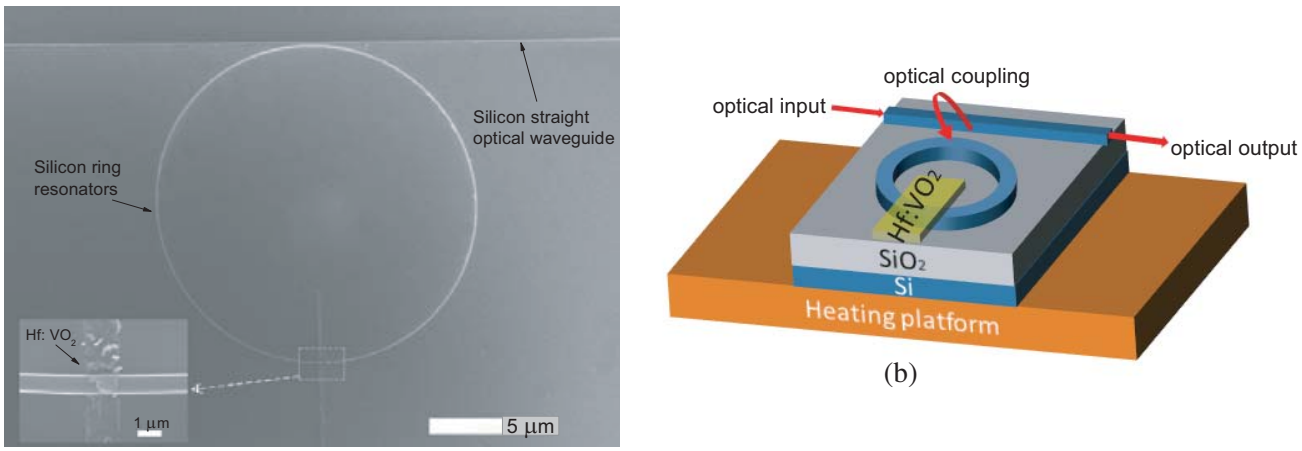

Figure 5. (a) SEM image of silicon ring resonator device partially covered by 3% Hf-doped vanadium oxide thin films. (b) The schematic characterization approach of the transmittance spectrum of the device. The heating of device was executed via a heating platform. After light inputting the silicon straight optical waveguide, the light of particular wavelength will be coupled into Silicon ring resonator device, causing no optical output of counterparts.

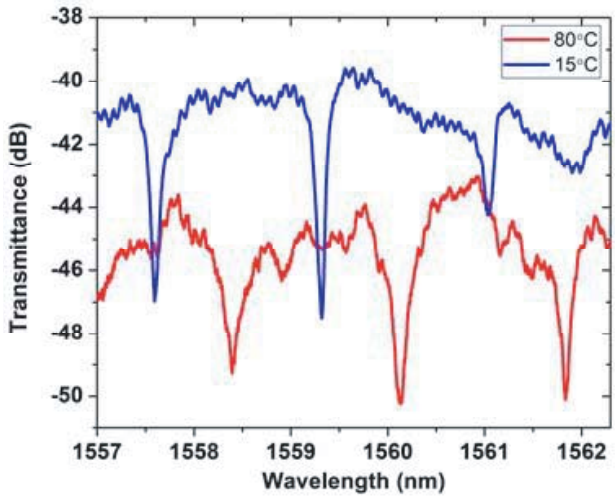

Figure 6. Resonance peaks at device temperatures of 15°C and 80°C.

Table 1. The result comparison of the different author's work.

Author	Q-factor	Reference
Our work	8.3×10^3	/
C. Manolatou et al.	7.5×10^3	Ref. [5]
J. D. Ryckman et al.	$7.8–8.8 \times 10^3$	Ref. [9]
M. S. Nawrocka et al.	6.7×10^3	Ref. [10]
J. Nag et al.	$10^2–10^3$	Ref. [11]

the quality factor changing from $Q = 12,600$ at 1559.3 nm at 15°C to $Q = 8,300$ at 1560.1 nm at 80°C, indicating a MIT process in Hf:VO_2(M1) causing metal phase induced extra loss to the ring resonator. The low order of magnitude 10^3 of Q-factor is close to the results of other work as shown in Table 1, and expected for applying in silicon photonic devices [9–11].

4. CONCLUSION

In summary, we fabricated Hf doped VO_2(M1) thin films for low power reconfigurable silicon photonic device applications. Doping Hf led to the negligible thermal hysteresis of the VO_2 thin films during MIT, and it maintained the tunability of resistivity and optical property in the MIT process. A silicon ring resonator with partially capped Hf:VO_2(M1) thin films was fabricated, demonstrating resonance frequency tuned by Hf:VO_2 phase transition. The narrow hysteresis in Hf:VO_2(M1) thin films allows accessing the intermediate phase transition states of the VO_2 material, making this material a promising candidate for silicon photonic device applications.

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