Reduced extrinsic recombination process in anatase and rutile TiO$_2$ epitaxial thin films for efficient electron transport layers

Yeon Soo Kim, Hye-Jin Jin, Hye Ri Jung, Jihyun Kim, Bich Phuong Nguyen, Juran Kim & William Jo*  

TiO$_2$ is the most widely used material for the electron transport layers (ETLs) because it is characterized by proper band alignment with light absorbers, adequate optical transmittance, and high electron mobility. There are two thermodynamically stable crystal phases of TiO$_2$: anatase and rutile. However, understanding which phase is more effective as the ETL is still required. In this paper, we demonstrate the different effects of using epitaxial anatase TiO$_2$ and epitaxial rutile TiO$_2$ (both grown using pulsed laser deposition) as the ETL material on the electrical and optical properties. Epitaxial Nb-doped TiO$_2$ layers were used as the common electrode material for both epitaxial phases for the crystalline structural analysis revealed high crystalline qualities and good coherency for both phases. By analyzing the recombination kinetics, the anatase phase shows a preferable performance in comparison with the rutile phase, although both epitaxial phases show remarkably reduced extrinsic recombination properties, such as trap-assisted recombination. This study demonstrates not only a better electron transporting performance of anatase phase but also reduced extrinsic recombination through epitaxy growth.

TiO$_2$ is a wide band gap semiconductor, one of the most extensively used transition metal oxide materials due to its various applications in, for example, light-emitting diodes, photocatalysts, solar cell conversion devices, high-k gate insulators, and waveguides. These various applications are strongly dependent on the different characteristics associated with each of the three crystal phases of TiO$_2$: anatase, rutile, and brookite. However, because the brookite polymorph is the most unstable phase due to its complex structure, most of the practical applications and research involve the thermodynamically stable anatase and rutile phases. There have been numerous studies on the comparison between the anatase and rutile phase, including those regarding the optical properties and photocatalytic activity so far. In addition, it is well-known that the TiO$_2$ satisfies most of conditions for the solar cell application, which having proper band alignment with the solar cell absorber layers for the efficient transporting of electrons and blocking of holes, adequate optical transmittance as well as high electron mobility to extract carriers from the light absorber layer and avoid charge recombination.

Although TiO$_2$ is currently the most commonly used electron transport layer (ETL) material in most of the solar cell applications, however, there is still debate as to whether the anatase or the rutile phase is more effective as an ETL in the solar cell application, such as dye-sensitized solar cells (DSSCs) and halide perovskite solar cells (HPSCs). The main reason for this debate is that the formation of the crystalline phase is not performed in a manner similar to that of a single crystal because most TiO$_2$ ETLs are deposited by spin coating, pyrolysis, or sputtering, which is advantageous for large-area fabrication of thin films. As a result, there is a lack of research on the difference between the anatase phase and the rutile phase, and understanding this difference could minimize the various defects formed in the ETL, such as oxygen vacancies and grain boundaries due to an amorphous-like polycrystalline structure. In particular, a factor of which a direct comparison could prevent the occurrence of these various defects in the anatase and rutile phase is trap-assisted recombination. Extrinsic recombination losses cause an unexpected open-circuit voltage drop that lowers the fill factor and the resulting trap center affects the long-term stability that causes the defect-induced degradation of the solar cell. Therefore, a nearly defect-free single crystalline phase of anatase and rutile TiO$_2$ thin films are a prerequisite.

Department of Physics and New and Renewable Energy Research Center (NREC), Ewha Womans University, Seoul 03760, Korea. *email: wmjo@ewha.ac.kr
In this study, the single crystalline phase of anatase and rutile TiO₂ thin films were fabricated using pulsed laser deposition, which is disadvantageous for fabricating large-area thin films but provides excellent control of the growth condition to obtain a high-quality thin film. High-resolution X-ray diffraction (HR-XRD) and high-resolution transmission electron microscopy (HR-TEM) measurements show high crystalline qualities of anatase and rutile epitaxial thin films.

Results and discussion
Figure 1a,b shows the X-ray diffraction (XRD) pattern of epitaxial TiO₂ thin films grown on LaAlO₃ (001) and γ-sapphire (1102) single crystal substrates, respectively. The XRD results demonstrate that there is no secondary phase except for the anatase and rutile phase on the LaAlO₃ and γ-sapphire substrates, respectively. The lattice parameter c for the anatase TiO₂ thin film on the LaAlO₃ substrate is 9.495 Å, which is only a 0.2% lattice mismatch with bulk anatase TiO₂ (9.514 Å). Additionally, the lattice spacing in the [011] direction of epitaxial rutile TiO₂ thin film on the γ-sapphire substrate is 2.489 Å, which is very close to the 2.487 Å lattice spacing of bulk rutile TiO₂. The thickness of both films was measured by X-ray reflectometry to be approximately 40 nm (Fig. S1, Supplementary Information). Figure 1c,d shows the cross-sectional HR-TEM images of anatase TiO₂ thin film/LaAlO₃ and rutile TiO₂ thin film/γ-sapphire, respectively. Both phases show clearly observable crystal structures and interfaces between the substrates. The crystal orientations were determined to be anatase (004) // LaAlO₃ (001) and rutile (011) // γ-sapphire (1102) by their corresponding fast Fourier transform (FFT) patterns shown in the insets of Fig. 1c,d, respectively. The half-transparent red circles denote simulated diffraction pattern results. The estimated lattice spacings of anatase (100), (001), and (110) from the TEM images are 3.928 Å, 9.077 Å, 3.928 Å.
This implies that the anatase thin film has in-plane coherency with the substrate. The lattice spacings in rutile substrate as estimated from the TEM images, the lattice spacings of anatase {100}, {001}, and {110} were adjusted to 3.872 Å, 9.089 Å, and 3.562 Å, respectively, values of which are more comparable to those of the TEM results. For the electrical measurement of TiO2 thin films along the out-of-plane direction, the conductivity of the bottom electrode on the substrate is essential. The bottom electrode should have a small lattice mismatch with both the substrate and TiO2 thin film for the epitaxial growth of the TiO2 thin film; however, it is difficult to find a suitable electrode material with a small lattice mismatch with both the LaAlO3 (001) and γ-sapphire (1T 02) substrates. Several perovskite oxides are suitable as good electrode material on LaAlO3 substrates, such as La0.5Sr0.5CoO3 and LaNiO3, however, they have a large lattice mismatch with γ-sapphire substrates. In contrast, binary oxides, such as RuO2,13 have a small lattice mismatch with γ-sapphire substrates, but epitaxial growth on LaAlO3 substrates is difficult. Furthermore, using different electrodes on different substrates would hinder the direct comparison of the optoelectronic properties between anatase and rutile TiO2 thin films. The addition of dopants, however, may be an effective strategy. In previous studies, transition metal ions, such as Nb and Y, were used as dopants in TiO2 to produce efficient ETLs.14,15 In this study, 10 wt% Nb-doped TiO2 target was prepared to investigate charge transporting and dynamics in the epitaxial thin films, both with a 1.5 J cm−2 laser fluence, as bottom electrodes.

Figure 2a shows the resistivity as a function of laser fluence varying from 1.0 to 1.5 J cm−2, with a lower laser fluence leading to more metallic films. In a previous study,16 increasing laser fluence lead to the preferential ablation of lighter atoms, or Ti atoms in this case, whereas decreasing laser fluence resulted in relatively Nb-abundant thin films. Additionally, the XRD pattern in the inset of Fig. 2a suggests that the diffraction peak of the Nb-doped TiO2 (004) is located at a lower angle than that of the TiO2 (004) peak. This peak shift indicates a lattice expansion of the Nb-doped TiO2 thin film of approximately 0.5%. The lattice expansion is observed in TiO2 epitaxial thin films, both with a 1.0 J cm−2 laser fluence leading to more metallic films. In a previous study,16 increasing laser fluence lead to the preferential ablation of lighter atoms, or Ti atoms in this case, whereas decreasing laser fluence resulted in relatively Nb-abundant thin films. Additionally, the XRD pattern in the inset of Fig. 2a suggests that the diffraction peak of the Nb-doped TiO2 (004) is located at a lower angle than that of the TiO2 (004) peak. This peak shift indicates a lattice expansion of the Nb-doped TiO2 thin film of approximately 0.5%. The lattice expansion is observed in TiO2 epitaxial thin films, both with a 1.0 J cm−2 laser fluence leading to more metallic films. In a previous study,16 increasing laser fluence lead to the preferential ablation of lighter atoms, or Ti atoms in this case, whereas decreasing laser fluence resulted in relatively Nb-abundant thin films. Additionally, the XRD pattern in the inset of Fig. 2a suggests that the diffraction peak of the Nb-doped TiO2 (004) is located at a lower angle than that of the TiO2 (004) peak. This peak shift indicates a lattice expansion of the Nb-doped TiO2 thin film of approximately 0.5%. The lattice expansion is observed in TiO2 epitaxial thin films, both with a 1.0 J cm−2 laser fluence leading to more metallic films. In a previous study,16 increasing laser fluence lead to the preferential ablation of lighter atoms, or Ti atoms in this case, whereas decreasing laser fluence resulted in relatively Nb-abundant thin films. Additionally, the XRD pattern in the inset of Fig. 2a suggests that the diffraction peak of the Nb-doped TiO2 (004) is located at a lower angle than that of the TiO2 (004) peak. This peak shift indicates a lattice expansion of the Nb-doped TiO2 thin film of approximately 0.5%. The lattice expansion is observed in TiO2 epitaxial thin films, both with a 1.0 J cm−2 laser fluence leading to more metallic films. In a previous study,16 increasing laser fluence lead to the preferential ablation of lighter atoms, or Ti atoms in this case, whereas decreasing laser fluence resulted in relatively Nb-abundant thin films. Additionally, the XRD pattern in the inset of Fig. 2a suggests that the diffraction peak of the Nb-doped TiO2 (004) is located at a lower angle than that of the TiO2 (004) peak. This peak shift indicates a lattice expansion of the Nb-doped TiO2 thin film of approximately 0.5%. The lattice expansion is observed in TiO2 epitaxial thin films, both with a 1.0 J cm−2 laser fluence leading to more metallic films. In a previous study,16 increasing laser fluence lead to the preferential ablation of lighter atoms, or Ti atoms in this case, whereas decreasing laser fluence resulted in relatively Nb-abundant thin films. Additionally, the XRD pattern in the inset of Fig. 2a suggests that the diffraction peak of the Nb-doped TiO2 (004) is located at a lower angle than that of the TiO2 (004) peak. This peak shift indicates a lattice expansion of the Nb-doped TiO2 thin film of approximately 0.5%. The lattice expansion is observed in TiO2 epitaxial thin films, both with a 1.0 J cm−2 laser fluence leading to more metallic films. In a previous study,16 increasing laser fluence lead to the preferential ablation of lighter atoms, or Ti atoms in this case, whereas decreasing laser fluence resulted in relatively Nb-abundant thin films. Additionally, the XRD pattern in the inset of Fig. 2a suggests that the diffraction peak of the Nb-doped TiO2 (004) is located at a lower angle than that of the TiO2 (004) peak. This peak shift indicates a lattice expansion of the Nb-doped TiO2 thin film of approximately 0.5%. The lattice expansion is observed in TiO2 epitaxial thin films, both with a 1.0 J cm−2 laser fluence leading to more metallic films. In a previous study,16 increasing laser fluence lead to the preferential ablation of lighter atoms, or Ti atoms in this case, whereas decreasing laser fluence resulted in relatively Nb-abundant thin films. Additionally, the XRD pattern in the inset of Fig. 2a suggests that the diffraction peak of the Nb-doped TiO2 (004) is located at a lower angle than that of the TiO2 (004) peak. This peak shift indicates a lattice expansion of the Nb-doped TiO2 thin film of approximately 0.5%.
where \( \tau_1 \) and \( \tau_2 \) denote the time for the slow delayed recombination at the trap center and the bimolecular recombination, which occurred on a relatively short time scale, respectively. The delayed recombination component and the bimolecular recombination component of the anatase TiO\(_2\) thin film was 17.83 ns and 1.45 ns, respectively, whereas the delayed and bimolecular recombination was 16.35 ns and 2.37 ns for the rutile TiO\(_2\) thin films, respectively. It can be observed that the amplitude of the bimolecular decay component is much larger than that of the slow decay (Table 1). The near absence of non-radiative recombination gives rise to the shortest reported average decay component, which can be expressed as

\[
\tau_{AVG} = \frac{\sum_i A_i \tau_i^2}{\sum_i A_i \tau_i}.
\]

This implies that electrons are effectively extracted from the absorber layer to the ETL without significant non-radiative recombination effect by minimizing undesirable trap sites inside the bulk, particularly more so in the anatase phase rather than in the rutile phase. Interestingly, the bimolecular decay component of anatase and rutile Nb-doped TiO\(_2\) epitaxial thin films as ETLS is comparable to that of anatase and rutile TiO\(_2\) epitaxial thin films. Thus, the effects due to the phase difference between the anatase phase and the rutile phase appear to be more dominant than the effects due to the addition of Nb dopants.

To measure the PCE, Au/spiro-OMeTAD/perovskite on anatase Nb-doped TiO\(_2\) with a fluence of 1.5 J cm\(^{-2}\)/anatase Nb-doped TiO\(_2\) with a fluence of 1.0 J cm\(^{-2}\)/LaAlO\(_3\) substrate (anatase HPSC) and Au/spiro-OMeTAD/perovskite on rutile Nb-doped TiO\(_2\) with a fluence of 1.5 J cm\(^{-2}\)/rutile Nb-doped TiO\(_2\) with a fluence of 1.0 J cm\(^{-2}\)/γ-sapphire substrate (rutile HPSC) were prepared as shown in Fig. 4a. A 250-μm-sized Au top
The electrode was deposited by an e-beam evaporator with a thickness of 40 nm. The current–density voltage ($J-V$) curves are shown for the different phases of the ETL (Fig. S6, Supplementary Information). It can be observed that the HPSC with the anatase phase demonstrates a better performance compared with the HPSC with the rutile phase. Additionally, the anatase HPSC exhibits a lower series resistance and higher shunt resistance compared to that of rutile HPSC (Fig. S7, Supplementary Information). There are several reasons for the unexpectedly low PCE. First, the high resistivity of the bottom electrode (~ $10^{-2} \, \Omega \, \text{cm}$) compared with conventional transparent conducting oxides, such as ITO (~ $10^{-4} \, \Omega \, \text{cm}$)$^{31}$, leads to high series resistance. Second, light incident on the rear contact is partially blocked by the Au electrode as shown in Fig. 4a. In addition, the electrical measurement is performed with probing contacts at the probe-station, which also blocked some of the incident light.

The open-circuit voltage ($V_{OC}$) is an important factor not only to determine the efficiency of the solar cell but also to investigate carrier recombination properties$^{32,33}$. To obtain reliable $V_{OC}$ data under an open-circuit condition, we measured the $V_{OC}$ as average readouts of a repeatedly applied current of ± 1 nA. Open-circuit voltage decay (OCVD)$^{33}$ measurements were performed by recording the $V_{OC}$ as a function of time (Fig. 4b). When the light illumination was switched off at $t=0$, the photo-induced electrons exponentially decayed due to the recombination process corresponding to the electron lifetime. The electron lifetime can be obtained using the following equation$^{33}$:

$$\tau_n = -\frac{k_BT}{e} \left[ \frac{dV_{OC}}{dt} \right]^{-1},$$

where $k_BT$ is the thermal energy and $e$ is the elementary charge. The electron lifetime derived from the OCVD results as a function of time is depicted in the inset of Fig. 4b, which shows that the anatase phase clearly demonstrates a longer electron lifetime and slower recombination kinetics than that of rutile phase, results of which are consistent with those of the TRPL.

Figure 4c shows that the $V_{OC}$ of the anatase and rutile HPSCs varied linearly as a function of the logarithm of the light intensity and can be given by$^{34,35}$

$$V_{OC} = \frac{E_{gap}}{q} - \frac{k_BT}{q} \ln \left( \frac{1 - P}{B_L + B_{SRH}} N_e^2 \right),$$

where $E_{gap}$ is the energy gap, $P$ is the dissociation probability of the excitons, $G$ is the generation rate of the exciton, $N_e$ is the effective density of states, and $B_L$ and $B_{SRH}$ are the Langevin recombination strength and the Shockley, Read, and Hall (SRH) recombination strength, respectively, where the Langevin and SRH recombination...
denote bimolecular and trap-assisted recombination, respectively. Only the generation rate $G$ is proportional to the light intensity in this equation, in which the slope can be expressed in units of $k_B T/q$. Although the effective density of states of anatase ($N_{C, anatase} \sim 7.8 \times 10^{20} \text{ cm}^{-3}$) is larger than that of rutile ($N_{C, rutile} \sim 2.5 \times 10^{19} \text{ cm}^{-3}$), the slope of anatase (0.87 $k_B T/q$) is more gradual compared with that of rutile (1.05 $k_B T/q$). Considering that trap-assisted recombination is minimized due to epitaxy growth, the lower bimolecular recombination strength in the anatase phase is in good agreement with the TRPL and OCVD results.

Also, effect of shunt resistance and RC-effect should be considered due to their substantial effect on open circuit voltage characteristics. Low shunt resistance gives rise to rapidly decrease of OCVD signal generally within a very short time scale, such as few seconds, however, their decay lasted up to several tens of seconds in

Figure 4. Electrical properties of the HPSC with different ETLs. (a) Schematic of the HPSC under illumination. (b) OCVD decay curves of the HPSC with different ETLs using the anatase or rutile phase on a semi-log scale. Inset of (b) shows the electron lifetime on a log–log scale from Eq. (2). (c) $V_{OC}$ as a function of the light intensity on a semi-log scale.

this experiment. In addition, the lower shunt resistance leads to the higher slope in the $V_{oc}$ vs light intensity$^{39}$. Although the anatase phase has lower shunt resistance (Fig. S7, Supplementary Information), it shows lower slope than of the rutile phase as seen in Fig. 4c. Furthermore RC-effect due to large time constant could over-estimated carrier life time$^{40}$. Although larger dielectric permittivity$^{41}$ and the series resistance (Fig. S7, Supplementary Information) of the rutile phase, however, longer carrier lifetime is observed in the anatase phase as seen in the inset of Fig. 4b. Therefore, we believe that the shunt resistance and the RC-effect do not have a considerable effect on the open circuit voltage characteristics. Moreover, surface trap-assistant recombination could lower slope less than $k_BT/q$ $^{42,43}$, accompanying with significantly reduce of open circuit voltage as well$^{44}$. However, since the open circuit voltage of the anatase phase shows higher than that of the rutile phase for entire light intensities in Fig. 4c, thus we believe that the surface trap-assistant recombination has no significant influence on the interface between the halide perovskite layers and the epitaxial electron transport layers.

Previous studies have demonstrated the better photo-induced activity of the anatase phase than of the rutile phase in terms of deeper bulk-to-surface carrier excitation$^2$, smaller effective mass$^3$, and indirect band structures$^5$. Other key parameters to maintain that can increase the PCE include a small conduction band offset, particularly to improve the open circuit voltage$^6$, and a smooth surface to reduce internal light scattering$^4$. To investigate the surface morphology and work function difference, we measured the topography and contact potential difference (CPD) simultaneously with atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM)$^{47,48}$. Figure 5a,b represents the surface morphology of anatase and rutile Nb-doped TiO$_2$ thin films, respectively. Their root-mean-square of roughness is approximately 0.9 nm and 6.6 nm for the anatase Nb-doped TiO$_2$ thin films and rutile thin films, respectively, indicating that the anatase thin film is particularly suitable for minimizing light scattering at the interfaces. The insets of Fig. 5a,b represent the mapping of the CPD of the
anatase Nb-doped TiO₂ thin films and rutile Nb-doped TiO₂ thin films, respectively. The CPD originates from the potential difference between the tip of the cantilever and the surface of the sample. The obtained CPD distribution histogram of the anatase and rutile Nb-doped TiO₂ thin films are shown in Fig. 5c. The measured work function difference is ~ 0.4 eV, which is consistent with previous results. Figure 5d displays the band diagrams of different electron extraction behavior from perovskite to the anatase and rutile phase under illumination.

Conclusions
In summary, we have deposited epitaxial anatase and rutile TiO₂ thin films as ETL for HPSCs. The structural analysis indicates that the films’ single phase possesses high crystalline qualities. Conducting epitaxial Nb-doped TiO₂ was prepared as a cathode by modulating the laser fluence. In comparison with the rutile phase, the anatase phase shows superior electrical and optical characteristics. The photoluminescence and open-circuit voltage analyses demonstrate that both the anatase and rutile phases show minimized trap-assisted recombination. This reduced trap-assisted recombination is a direct indication of the reduced trap density, which is highly correlated to long-term stability. In particular, the anatase phase has lower recombination properties likely due to having better band alignment and a flatter surface that results in lower light scattering at the interface. We believe that epitaxial growth-based single-phase studies not only demonstrate the surpassing properties of the anatase phase but also have the potential to significantly extend into the long-term stability through reduced extrinsic recombination in the future.

Methods
Epitaxial thin film preparation. We deposited epitaxial anatase and rutile TiO₂ thin films on LaAlO₃ and y-sapphire 0.5-mm-thick single-crystal substrates, respectively, using the pulsed laser deposition technique with an oxygen partial pressure of 100 mTorr at a temperature of 750 °C. The repetition of the laser was 5 Hz and 2 Hz with a laser fluence of 1 J cm⁻² and 1.5 J cm⁻², respectively.

Halide Perovskite precursor preparation. The detailed procedures are described in a study by Saliba et al. First, we prepared 1.5 M stock solutions of PbI₂, PbBr₂, and RbI in dimethylformamide (DMF): dimethyl sulfoxide (DMSO) with 4:1 V/V and CsI in pure DMSO. The solutions were heated at 180 °C for 10 min to be fully dissolved. Methylammonium bromide (CH₃NH₃Br, MABr) and formamidinium iodide (NH₂CHNH₂I, FAI) powders were added to the stock solutions of PbBr₂ and PbI₂, respectively, to obtain an amount of slightly excessive PbI₂ with a stoichiometry of 1:1:09. Next, 0.75 mL of FAPl₂ and 0.15 mL of MAPbBr₃ solutions were combined to prepare the (FA)₀.₈₃(MAPbBr₃)₀.₁₇ precursor solution. As additives, 0.048 mL of CsI and 0.052 mL of RbI from the stock solutions were added.

HPSC fabrication. The resulting halide perovskite solution was coated onto the epitaxial anatase and rutile thin films by a sequential two-step spin-coating, in which the spin rate of the first step was 1000 rpm for 10 s with an accelerated speed of 200 rpm/s and the spin rate of the second step was 6000 rpm for 20 s with an accelerated speed of 2000 rpm/s. At the end of the 15 s during the second step, 200 µl of chlorobenzene as the antisolvent was dropped into the center of the substrate. Then, the films were moved onto a pre-heated hot plate and annealed at 100 °C for 50 min.

After cooling down to room temperature, the HTL solution was dropped during spinning on top of the thin film by spin coating at 4000 rpm for 10 s using a chlorobenzene solution containing Spiro-OMeTAD (50 mg in 0.498 mL), which included as additives 0.018 mL of 4-tert-butylpyridine, 0.010 mL of 1.8 M lithium bis(trifluoromethanesulfonyl)imide stock solution, and 0.004 mL of 0.25 M tris(2-(1H- pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III) tri[bis-(trifluoromethane)sulfonimide] (FK209) stock solution.

HPSC characterization. The J–V curves of the HPSCs were measured using a Keithley 4200 source meter under simulated 1-sun illumination at AM 1.5G, 100 mA·cm⁻² (Sol3A Class AAA, Oriel, Newport) in an ambient atmosphere at room temperature. The AFM topography and KPFM measurements were performed by a n-Tracer (Nano Focus) in non-contact mode. The steady-state PL spectra and TRPL curves were collected using a commercial time-correlated single-photon counting system (FluoTime 300, PicoQuant). XPS measurements were obtained with a Thermo Scientific K-Alpha spectrometer.

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Author contributions
Y.S.K. and W.J. wrote the manuscript and designed the experiments. Y.S.K. carried out most of the experiments, analyzed the data, drew all the schematics and interpreted the results. H.-J.J. contributed to fabrication of epitaxial thin films. H.R.J., J.K. and B.P.N. contributed to fabrication and characterization of HPSC. J.K. contributed to measurement of KPFM. W.J. supervised the project.

Competing interests
The authors declare no competing interests.

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Correspondence and requests for materials should be addressed to W.J.

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