Plasma modelling of non-reactive and reactive HiPIMS discharges for tungsten deposition

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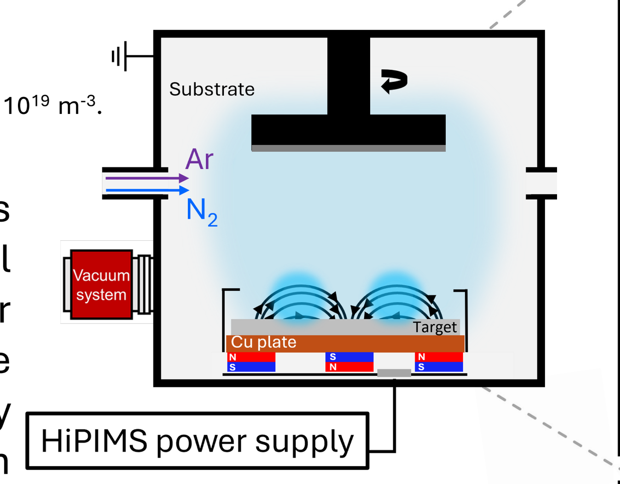
Reactive High Power Impulse Magnetron Sputtering

→ **Magnetron Sputtering**: technique used to deposit films and coatings with controlled composition and properties through the ejection of atoms from a target bombarded by energetic ions generated in a glow discharge, where electrons are confined by a suitably shaped magnetic field [1].

→ **Direct Current Magnetron Sputtering:**
- Plasma density ~ $10^{15} - 10^{17}$ m^{-3}.
- Constant discharge voltage.
- Low fraction of ionized sputtered species.

→ **High Power Impulse Magnetron Sputtering (HiPIMS)** [2]:
- Pulsed discharge voltage.
- Plasma density ~ $10^{18} - 10^{19}$ m^{-3}.
- High fraction of ionized sputtered species.



→ Reactive HiPIMS [2,3] introduces significant plasma-chemical complexity due to molecular dissociation, ionization and surface processes, yet it remains highly promising for the controlled growth of compounds films.

➡ **Modeling is essential to understand the process physics.**

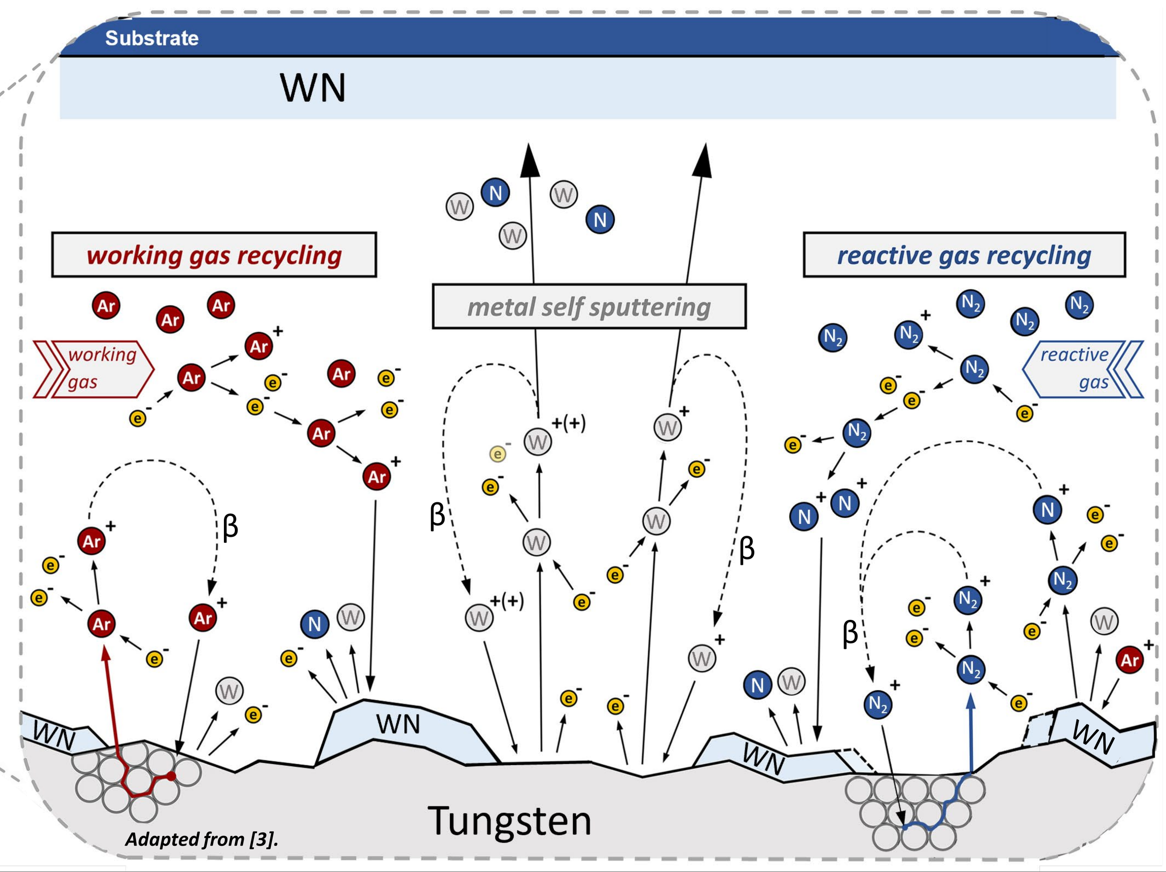
Ionization Region Model (IRM)

→ Time-dependent, zero-dimensional (volume-averaged) plasma chemistry model of the ionization region (IR) [3].

→ Evolution of plasma species and plasma parameters inside the IR. ➡ **Ordinary differential equations for**

- Electron energy.
- Particles density.

$$\frac{dT_e}{dt} = \sum Q_{abs} - \sum Q_{loss} \qquad \frac{dn_i}{dt} = \sum R_i^{generation} - \sum R_i^{loss}$$



→ Experimental input parameters (e.g., discharge current $I_D(t)$).

→ **$I_D(t)$ reproduced using two fitting parameters**:
1. Fraction of the total discharge power which goes to energizing the electrons (f_{pwr}).
2. Back-attraction for ionized species (β).

→ **The calculated current is**:

$$I_{calc} = e \sum S_{RT} Z_i \Gamma_i^{RT} (1 + \gamma_{eff,i})$$

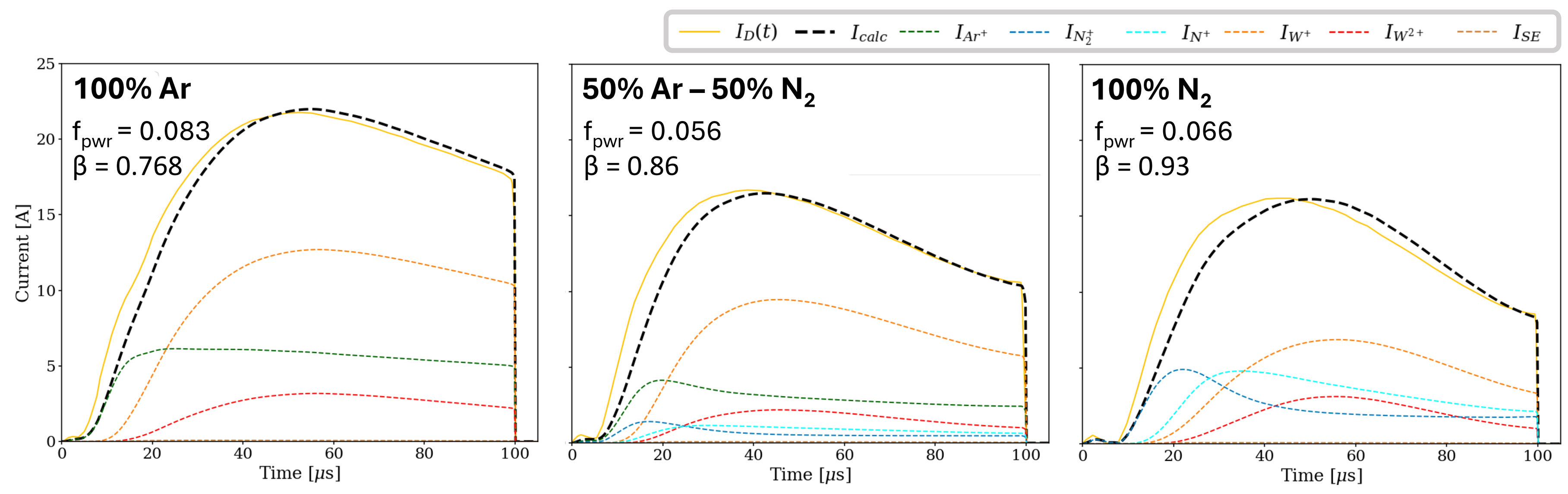
→ To extend the IRM model to the reactive regime, it must account for target poisoning, mixed sputtering from metal and compound and their different secondary electron emission properties [4,5].

Model implementation and fitting: HiPIMS tungsten discharge

→ Three different HiPIMS discharges with a tungsten target were investigated while varying the working gas composition: 100% Ar, 50% Ar – 50% N_2, and 100% N_2. In all cases, the pressure was fixed at 0.5 Pa, the pulse duration and frequency were 100 µs and 175 Hz, respectively, and the average power was set to 200 W.

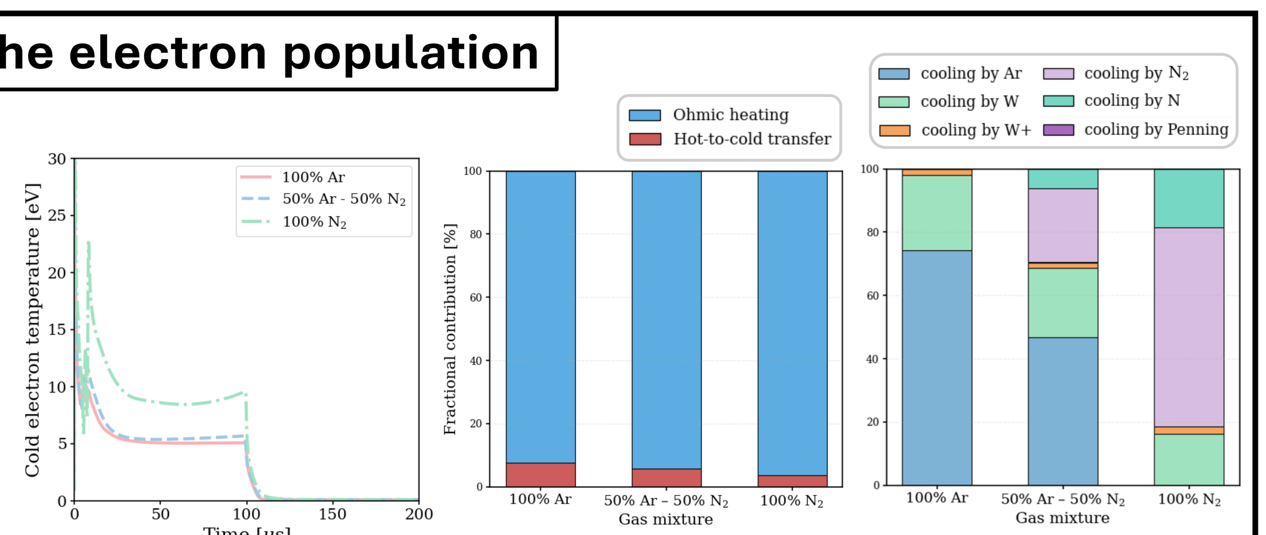
→ By optimizing the power fraction and back-attraction probability, the IRM achieves excellent agreement between calculated and experimental discharge currents across all gas mixtures.

→ Increasing N_2 content introduces complex dissociation and ionization pathways that consume more energy, resulting in a visible current onset delay and a significant reduction in peak amplitude



Heating and cooling of the electron population

→ Ohmic heating remains the dominant electron heating mechanism across all gas compositions, contributing over 90% of the total energy gain.



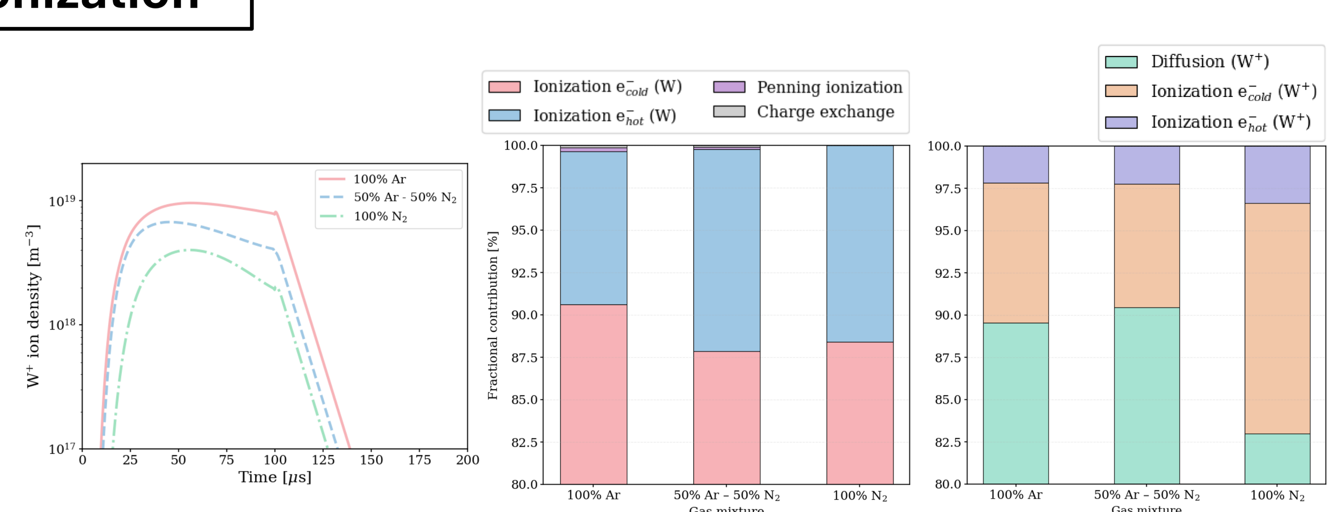
→ A marginal decrease in "Hot-to-cold" transfer is observed with N_2 addition, suggesting a reconfiguration of the electron energy distribution function (EEDF).

→ The transition from 100% Ar to 100% N_2 triggers a massive redistribution of energy sinks, where the dominance of Ar/W electronic excitation is superseded by nitrogen species.

→ The cooling profile in N_2 -rich discharges is dictated by the high-energy cost of molecular dissociation and excitations, which effectively clamp the electron temperature.

Sputtered species ionization

→ Direct electron impact by the "cold" electron population (e_{cold}) is the primary driver for tungsten ionization, accounting for approximately 90% of W^+ production across all gas mixtures.

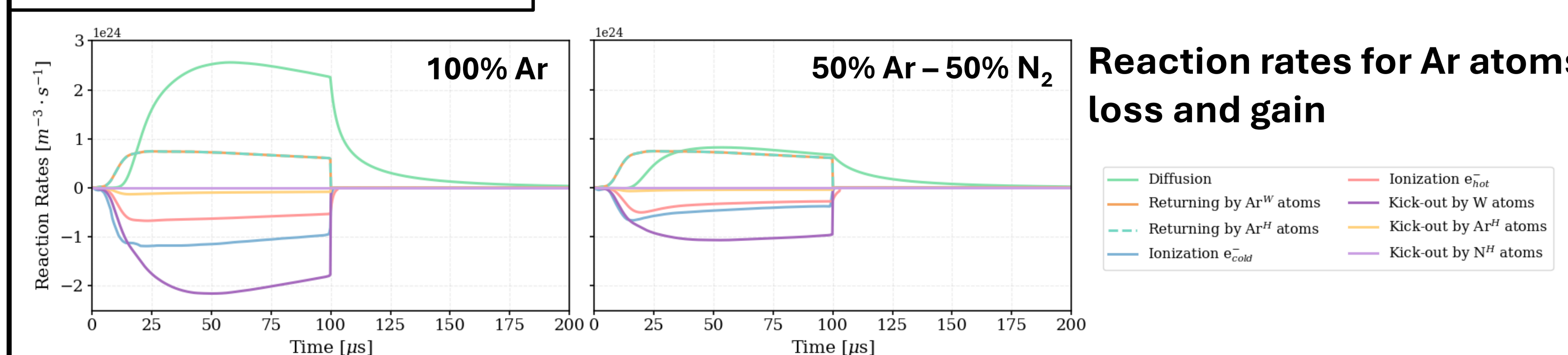


→ Secondary processes such as Penning ionization and charge exchange contribute negligibly, indicating that the neutral metal kinetics are almost exclusively controlled by the thermal electron distribution.

→ The depletion of W^+ ions is governed by the competition between spatial diffusion (out of the ionization region toward the racetrack and bulk plasma) and further ionization to W^{2+}.

→ A 100% N_2 atmosphere increases the fractional contribution of W^{2+} production, indicating that electron impact ionization becomes an increasingly dominant loss channel for W^+ compared to diffusion.

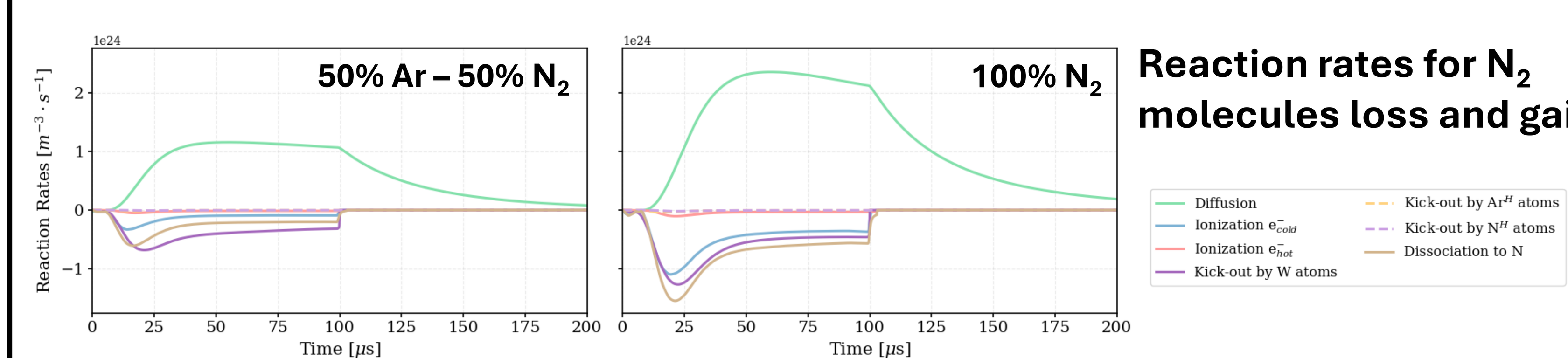
Gas atom loss and gain



Reaction rates for Ar atoms loss and gain

→ Competition between loss via electron-impact ionization or kick-out by energetic species ("sputtering wind") and a primary gain channel via the diffusion from the gas reservoir.

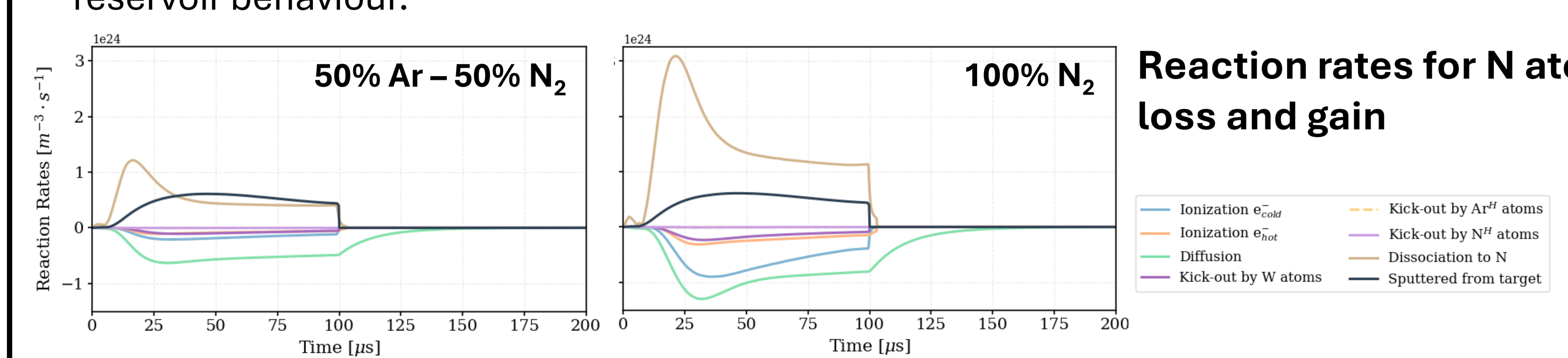
→ The introduction of N_2 balances the diffusion refill with a significant contribution from "warm" and "hot" Ar atoms returning from the target.



Reaction rates for N_2 molecules loss and gain

→ The molecular density loss is governed by dissociation into N atoms and kick-out by W atoms, which is offset by the positive gain of N_2 molecules diffusing from gas reservoir.

→ For the 100% N_2 atmosphere, the initial peak in dissociation represents the primary energy sink, while the refill from the bulk gas stabilizes at a lower rate compared to the pure Argon reservoir behaviour.



Reaction rates for N atoms loss and gain

→ Atomic N is generated as a net gain term through the dissociation of N2 and the sputtered contribution from the target, while diffusion and ionization act as the main loss channels.

→ In the 50% Ar – 50% N_2 mixture, N gain is nearly equally shared between dissociation and sputtering, whereas in the 100% N_2 case the dissociation of N_2 molecules becomes the overwhelmingly dominant production mechanism.

Conclusions & Foreseen Activities

→ The IRM provides a fundamental bridge between external discharge parameters and internal plasma chemistry, revealing that N_2 addition does not just fundamentally reconfigures the electron energy dissipation channels.

→ Cold electron temperature (T_e) is dynamically regulated by the gas composition. While pure Ar discharges reach a steady state quickly, the introduction of N_2 forces T_e to remain significantly higher to sustain the energy-intensive molecular dissociation and ionization pathways that replace noble gas electronic transitions as the primary cooling sinks.

→ The ionization of sputtered metal atoms is primarily driven by "cold" electron impact, while the balance of neutral gas species is maintained by a complex competition between gas reservoir refill and target-recycled species.

→ Correlate IRM model outputs with the resulting tungsten nitride (WN_x) film stoichiometry and microstructure.

→ Perform time-resolved Langmuir probe measurements to experimentally validate the T_e temporal evolution predicted by the model.

→ Couple the IRM results with a Monte Carlo transport code to track the spatial distribution of film-forming species as they move from the ionization region to the substrate.

References

[1] J. T. Gudmundsson, Plasma Sources Sci. Technol. 29 (2020).

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