Choline Hydroxide as a low-toxic, metal-ion-free alternative developer to TMAH for Photoresists and HSQ

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INTRODUCTION

TMAH (Tetramethylammonium hydroxide) is the standard developer for photoresists as well as e-beam resists like Medusa 84 SiH (HSQ).

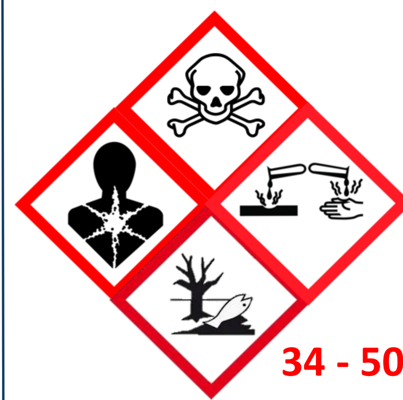
However, TMAH is **highly toxic** and poses considerable **health, safety and enviromental risks.**

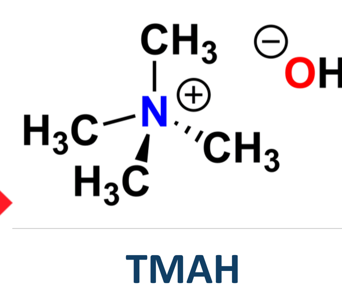
Choline hydroxide offers a **low-toxic, metal-ion free** alternative with improved performance for HSQ-based resists like Medusa 84 SiH.

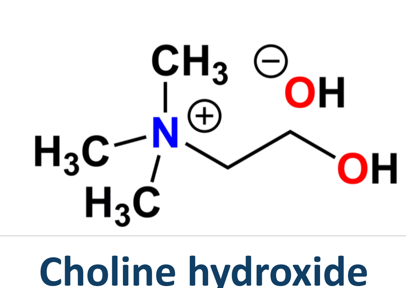
OUR GOAL

Replace hazardous TMAH with a safer, sustainable and high-performance alternative – without compromising process reliability or lithographic performance

CHEMICAL PROPERTIES







TMAH		Choline hydroxide
34 - 50 mg/kg (25 % TMAH)	LD50 (Rat) oral	4770 mg/kg (45 % chOH)
Fatal if swallowed or contact with skin Causes damage to the central nervous system	Chemical Safety	Causes skin burns and serious eye damage
Toxic to aquatic life with long lasting effects	Environmental Safety	readily biodegradable

Development performance of choline hydroxide in comparison with 2.38% TMAH

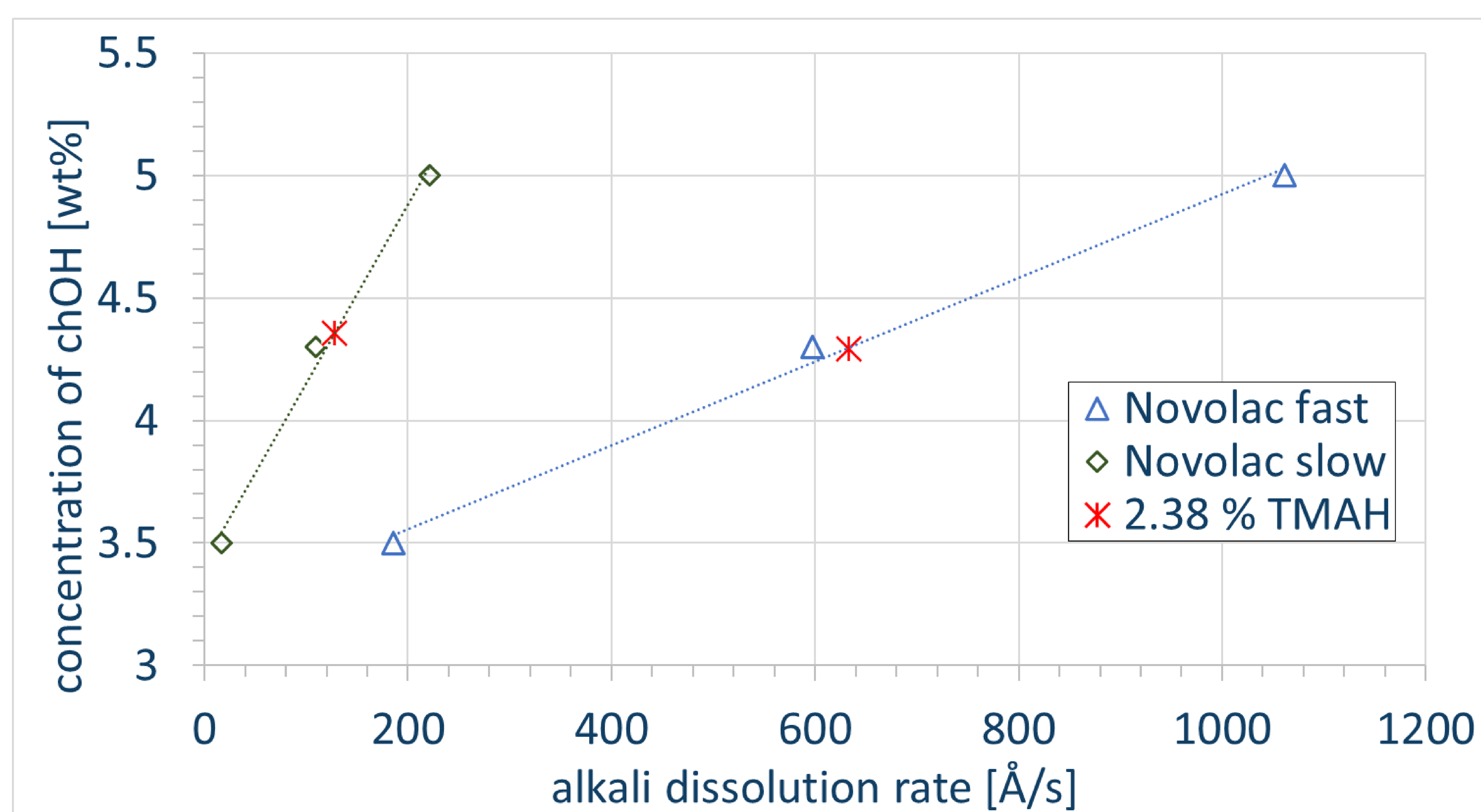


Figure 1: Alkali dissolution rates (ADR) in Angstrom per second for two different types of novolac at different chOH concentrations.

The best match for the dissolution rate of 2.38% TMAH falls within a narrow range of 4.3% to 4.35% chOH for slow- and fast-dissolving novolac resins.

Sensitivity of **positive resist AR-P 3250T** (DNQ-based, novolac slow, 10 µm)

- H_0^{60}: Minimum exposure dose required to fully developed layer within 60 sec.
- Higher dissolution enhancement of UV-exposed DNQ are observed with low concentrated chOH developers → stronger interaction with indene carboxylic acid.

Developer	2.38 % TMAH	3.11 % chOH	4.3 % chOH
mJ/cm² (H_0^{60} i-line)	371	386	385

Developing time of **negative resist AR-N 4400-50** (novolac fast, 50 µm)

- D_0^{90}: Development time with ≥90 % of exposed structures thickness remaining.
- Identical development speed for 2.38 % TMAH and 4.3 % chOH.
- Not fully developed structures after 10 min with 3.11 % chOH.

Developer	2.38 % TMAH	3.11 % chOH	4.3 % chOH
Developing time in sec. (D_0^{90})	255	-	250
	258	-	260

Development performance of choline hydroxide for Medusa 84 SiH (HSQ)

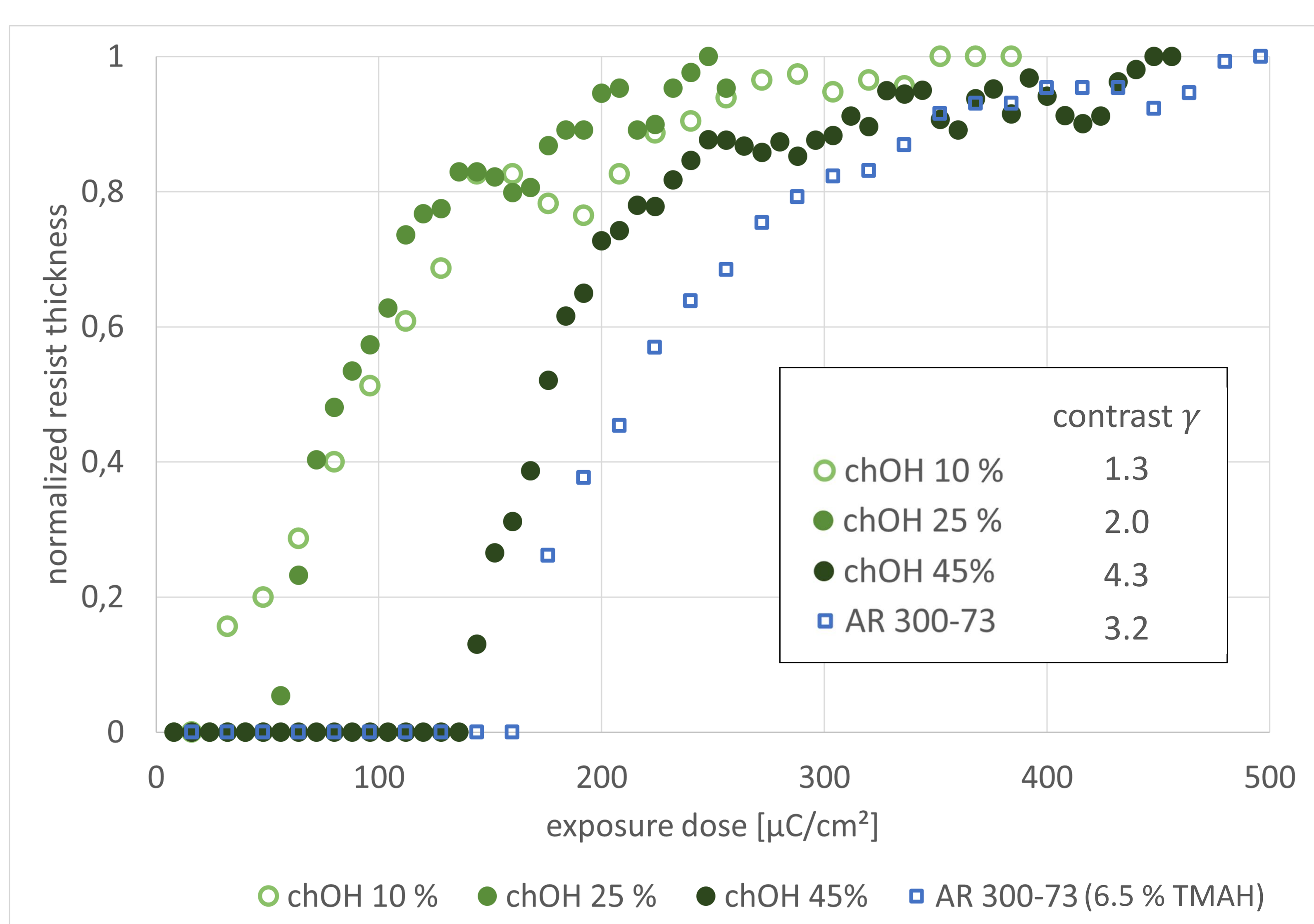


Figure 2: Contrast curves of Medusa 84 SiH developed with different concentrations of choline-hydroxide and 6.5% TMAH.

Process parameters for the resist **AR-N 8400.08**

- 6" Si, 4k rpm, 100 °C 60 sec HP, 100 nm layer thickness
- Vistec SB 254 variable-shape beam, 50 kV
- Immersion development 60 sec

✓ High sensitivity remains even at highest chOH concentrations.
✓ Increasingly higher contrast with increased chOH concentration.
✓ Contrast of γ = 4.3 with 45% chOH achievable – outperforming 6.5% TMAH.

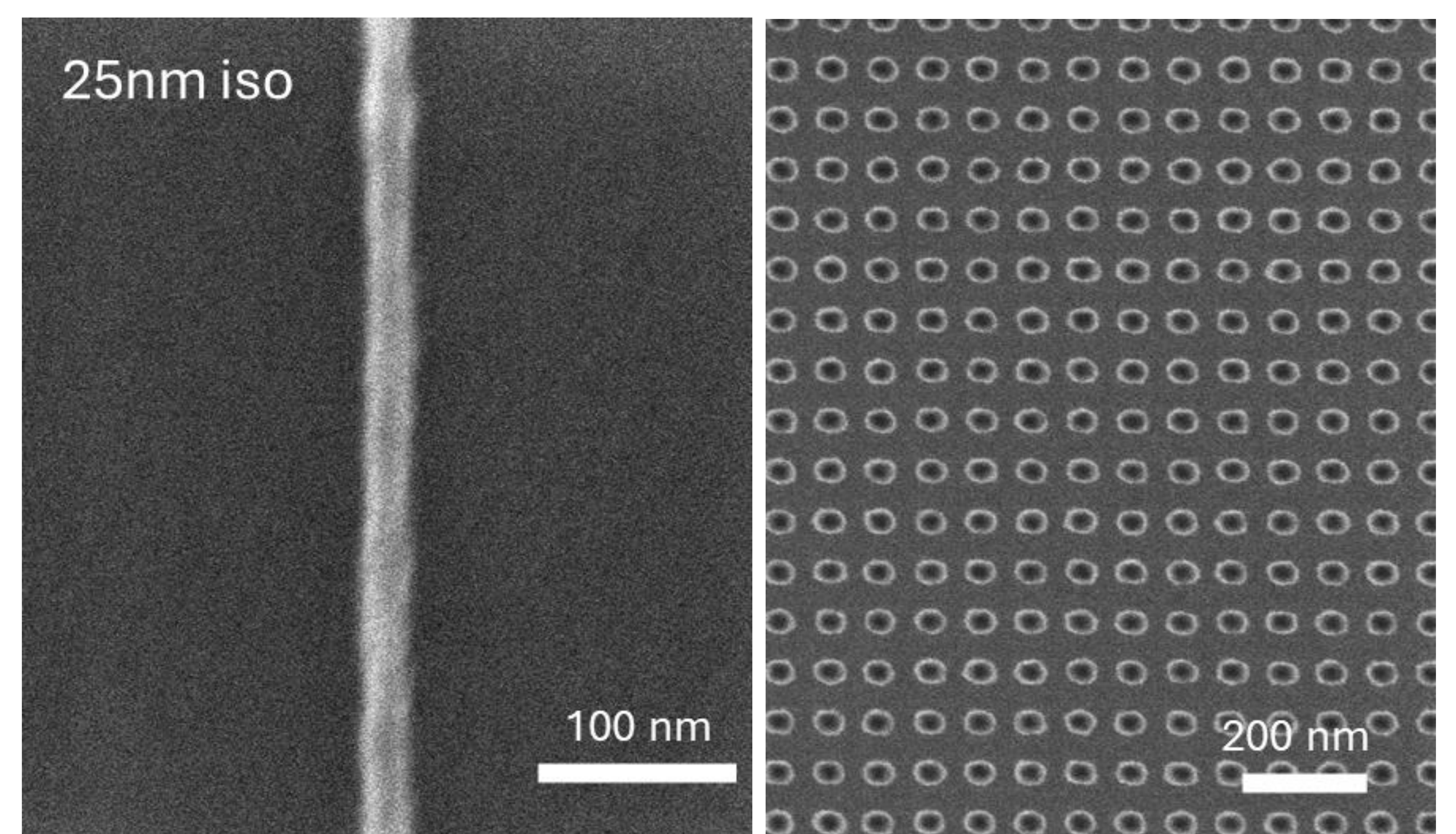


Figure 3 left: Single isolated 25 nm line written with 1800 µC/cm² and developed with 45 % chOH for 60 sec.

Figure 3 right: Square array of 80 nm dots with 160 nm pitch written with 520 µC/cm² and developed with 45 % chOH for 60 sec.

Outlook & Acknowledgements

Choline hydroxide shows strong potential as a safer and sustainable replacement for TMAH in advanced lithography processes.

Allresist GmbH offers choline-hydroxide-based developers within its developer portfolio under the product names AR 300-41 (45%) and AR 300-42 (4.3%)

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