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

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Tetramethylammonium hydroxide (TMAH) is the predominant metal-ion-free developer in semiconductor manufacturing, but its use is accompanied by significant acute oral and dermal toxicity. [1]. This toxicity presents substantial risks to operators, particularly in processes that are not fully enclosed or automated. Furthermore, the disposal of large volumes of TMAH-containing waste is subject to stringent environmental regulations. The identification of non-toxic, and metal-ion-free developer chemistries is therefore a desirable objective.

Choline hydroxide (Ch-OH) is a promising candidate due to its non-toxicity and strong basicity in aqueous solution [2]. The present study investigates the characteristics of the developer in the domains of positive and negative tone photoresists, as well as hydrogen silsesquioxane (HSQ).

When comparing the development speeds of TMAH and Ch-OH for novolac-based photoresists, the basicity of the aqueous solution is an important factor. TMAH is a very strong base with a pKa of ≈14, whereas Ch-OH is a slightly weaker base with a pKa of ≈11.5. In order to achieve the same development behavior as 2.38 % TMAH, various concentrations of Ch-OH were tested on the photoresists AR-N 4400-50 & AR-P 3250T (Allresist GmbH). Best results were obtained with concentrations between 4% to 4.3%.

Several developer chemistries for HSQ resists are known: salty developers based on NaOH/NaCl solutions [3], KOH as well as TMAH solutions with concentrations up to 25% [4]. The e-beam resist Medusa 84 SiH (Allresist GmbH) containing pure HSQ was used to compare the development characteristics of Ch-OH against TMAH- and KOH-based developers.

[1] https://pubchem.ncbi.nlm.nih.gov/compound/60966
[2] https://chem.echa.europa.eu/100.004.206/overview
[3] J. K. W. Yang, K. K Berggren, *J. Vac. Sci. Technol., B* **2007,** *25* 2025–2029.
[4] Y. M. Georgiev, et. al., *Vacuum* **2005,** *77*, 117–123.

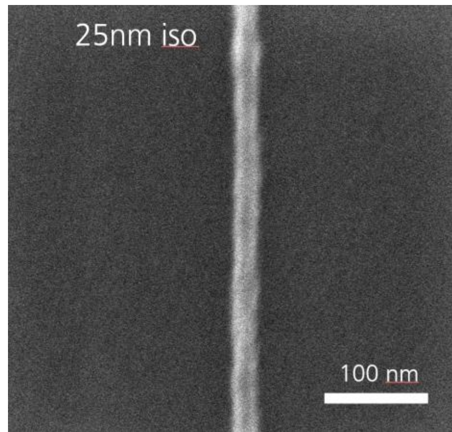

Figure 1: Isolated line written with 1800 µC/cm² at 50 kV using Medusa 84 SiH with a thickness of 130 nm; developed with 45% Ch-OH for 60 sec.

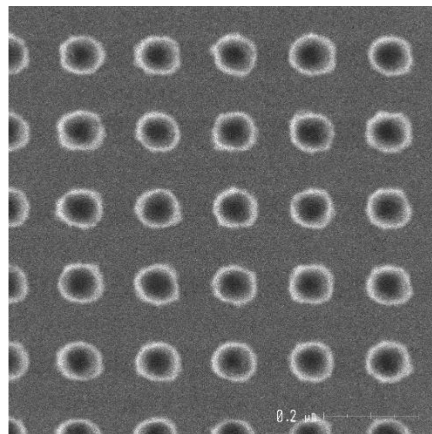

Figure 2: 80 nm dots 1:1 written with 720 µC/cm² at 50 kV using Medusa 84 SiH with a thickness of 130 nm; developed with 45% Ch-OH for 60 sec.