Tin cage photoresists for EUV lithography

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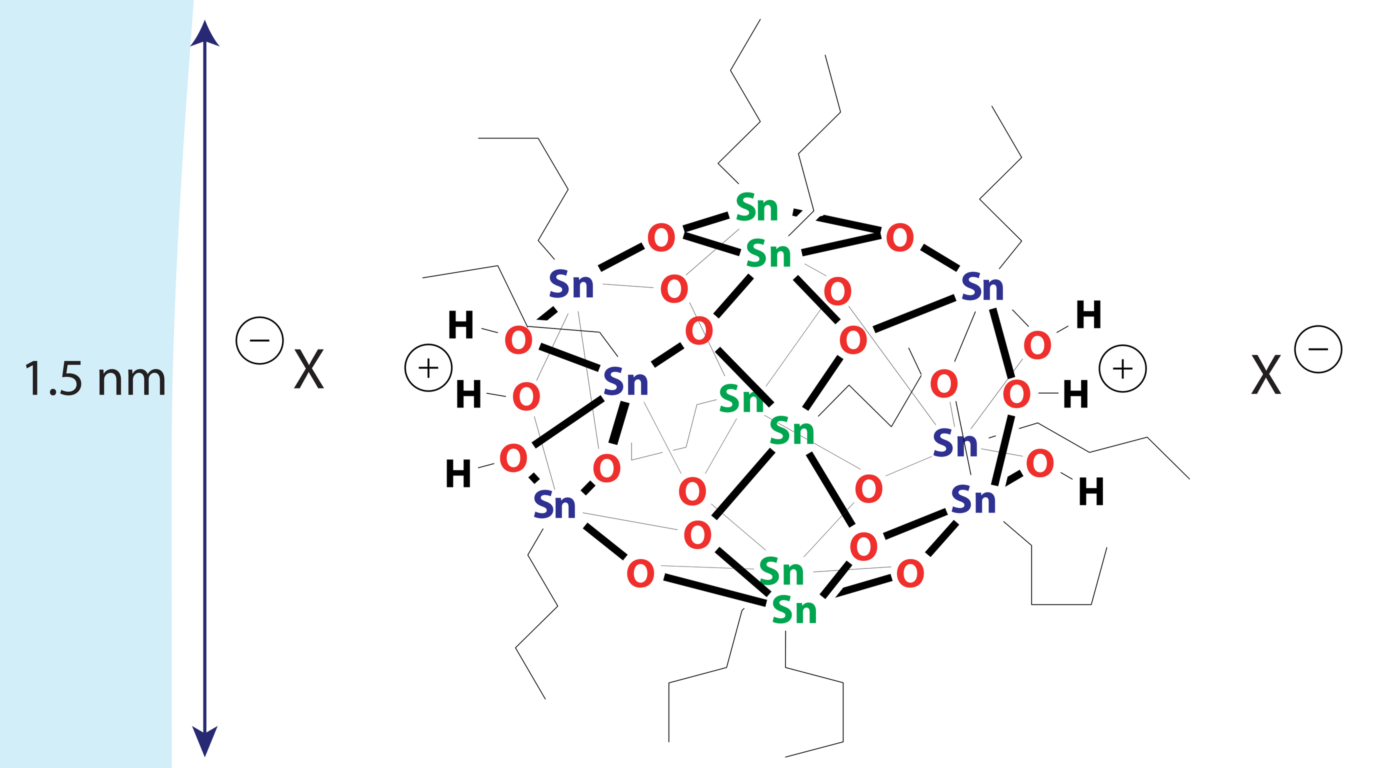
Introduction

A strong absorption of EUV light can be favorable for the sensitivity of a photoresist. Additionally, a higher number of absorbed photons reduces stochastic effects, which is beneficial for reducing line edge roughness (LER). Organometallic compounds are therefore interesting for use as photoresist materials, because their metal atoms strongly absorb EUV light. One of the metals with a large EUV absorption cross-section is tin (Sn). This work aims to provide insight into the EUV lithographic performance of an organometallic cage compound containing twelve Sn atoms.

Properties of the Sn_{12} cage molecule

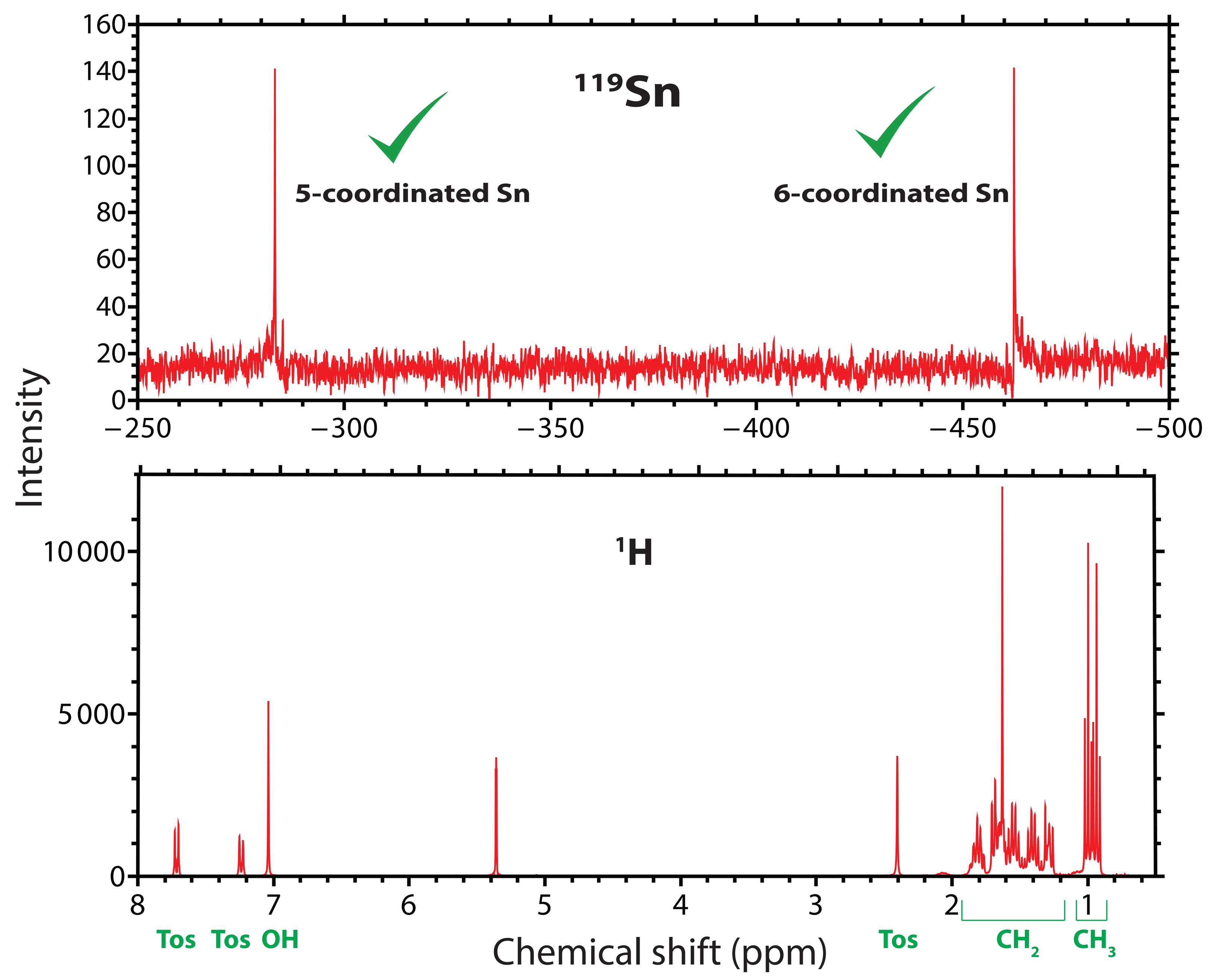


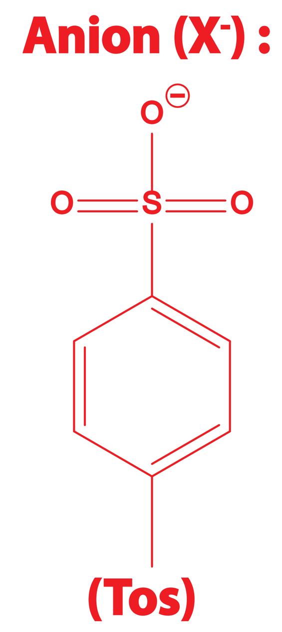
Small, well defined material with negative resist properties.[1]

Two types of Sn atoms:
- 5-coordinated **(green)**
- 6-coordinated **(blue)**

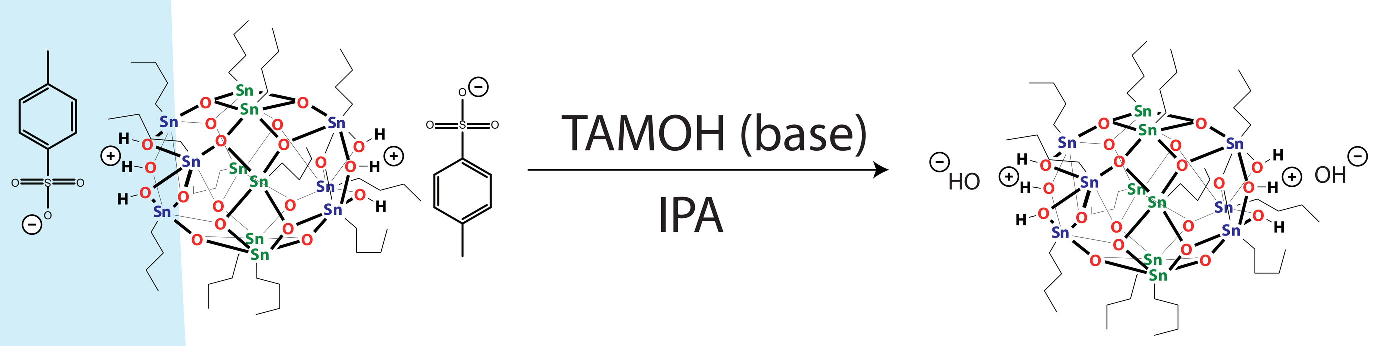
Positive charge (+1) located on each side of the cage: compensated by anion (X).[2]

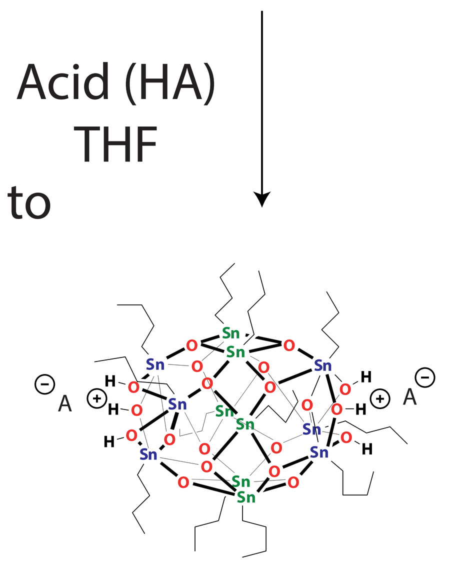
Confirming the chemical structure: ^{119}Sn and ^{1}H NMR





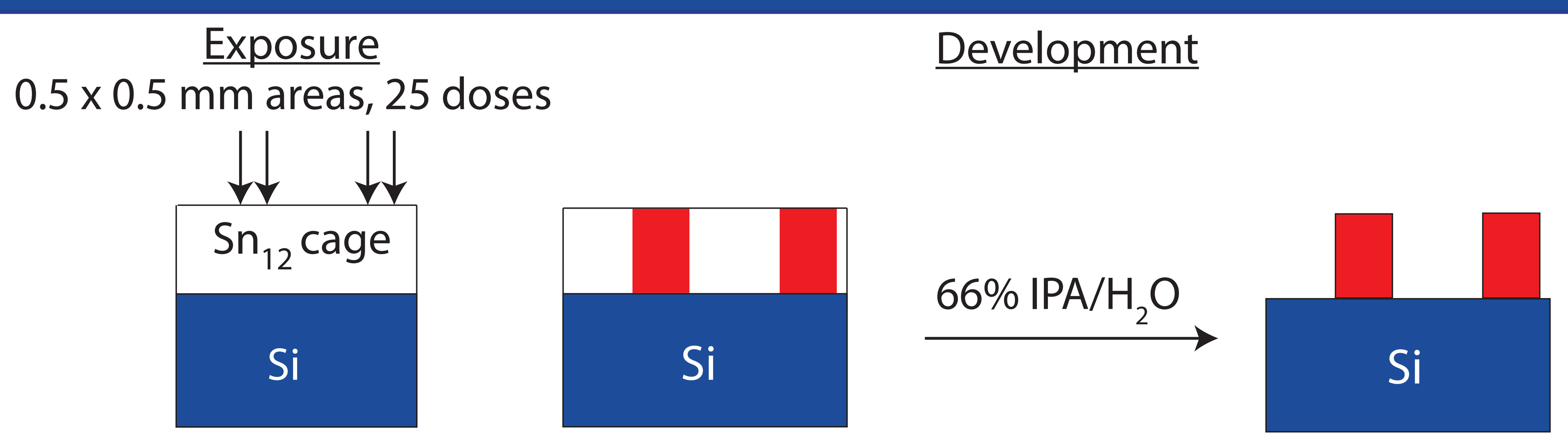
Anion exchange



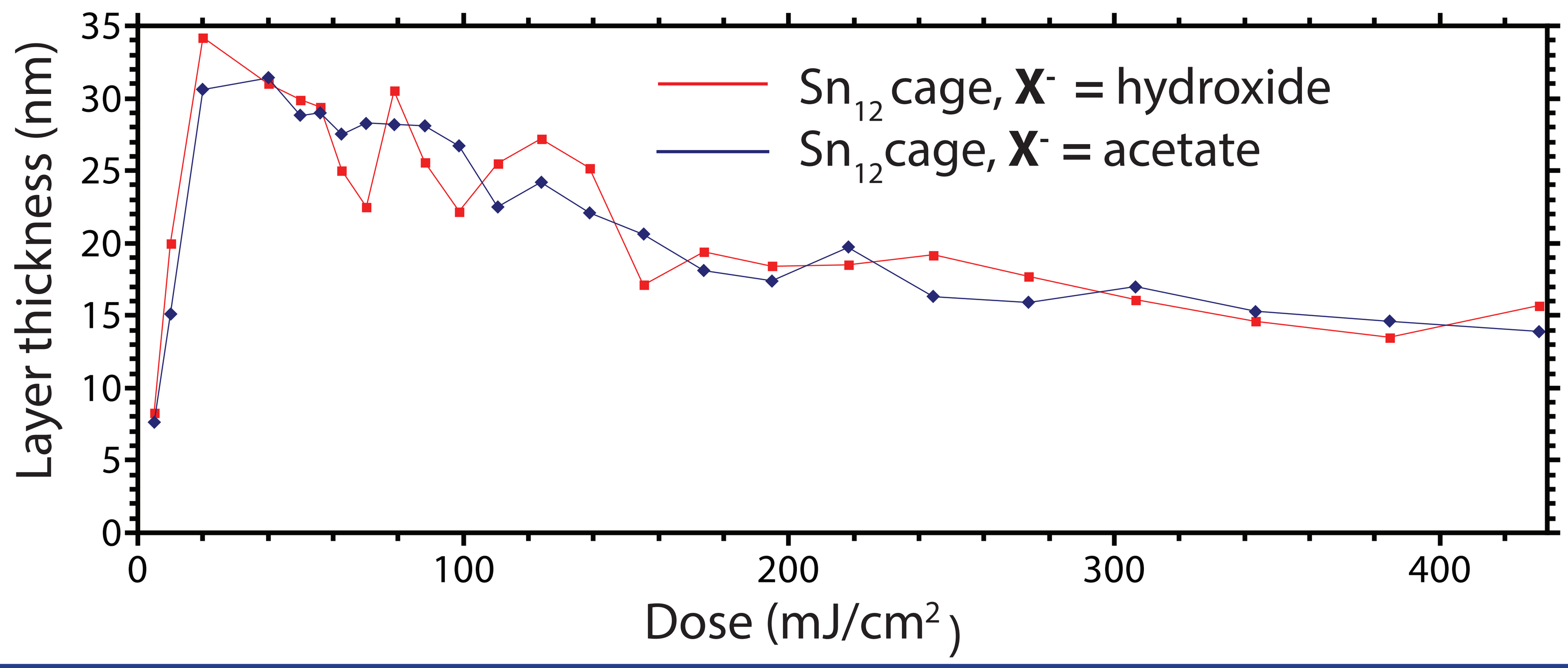


- Tosylate anions can be exchanged to hydroxides.
- Hydroxide form can be converted to other forms, using the corresponding acid (HA).

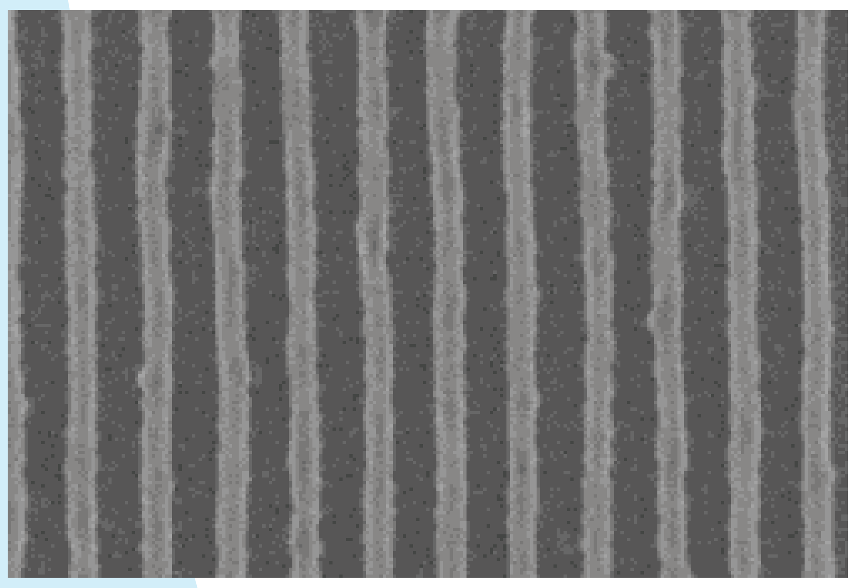
EUV contrast curves (H-D curves):



- Thickness analysis by AFM (step height measured).



EUV lithography pattern



141 mJ/cm², 35 nm HP lines

- Pattern collapse or other issues observed at 22 nm.
- Lines not completely resolved at lower dose (~70 mJ/cm²).

Results

- Smooth films were obtained by spin coating, although with some anions crystallization occurred (AFM imaging)
- All tin cage materials are quite sensitive: 20 mJ/cm² required for material conversion.
- A higher dose is required for good performance at the nanometer level. However, the used doses are lower than previously described.
- At higher EUV doses the films gradually decrease in thickness, probably because of loss of organic material
- Chemical mechanism behind solubility change is still unclear. However, exchanging the anions does not seem to alter the mechanism.

Acknowledgments

The authors thank Michaela Vockenhuber (PSI), Elizabeth Buitrago (PSI), Oktay Yildirim (ASML) and Aniket Thete (ARCNL) for their contribution to this work.

[1]B. Cardineau, Ryan Del Re , Miles Marnell, Hashim Al-Mashat, Michaela Vockenhuber, Yasin Ekinci, Chandra Sarma, Daniel A. Freedman, Robert L. Brainard, Photolithographic properties of tin-oxo clusters using extreme ultraviolet light (13.5 nm) , *Microelectron. Eng.* (2014)

[2]C. Eychenne-Baron, F. Ribot, and C. Sanchez. New synthesis of the nanobuilding block $[(BuSn)_{12}O_{14}(OH)_6]^{2+}$ and exchange properties of $[(BuSn)_{12}O_{14}(OH)_6](O_3SC_6H_4CH_3)_2$. *J. Organomet. Chem.* (1998)

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