Alkyltin Keggin Clusters as a Photoresist Material for EUV Lithography

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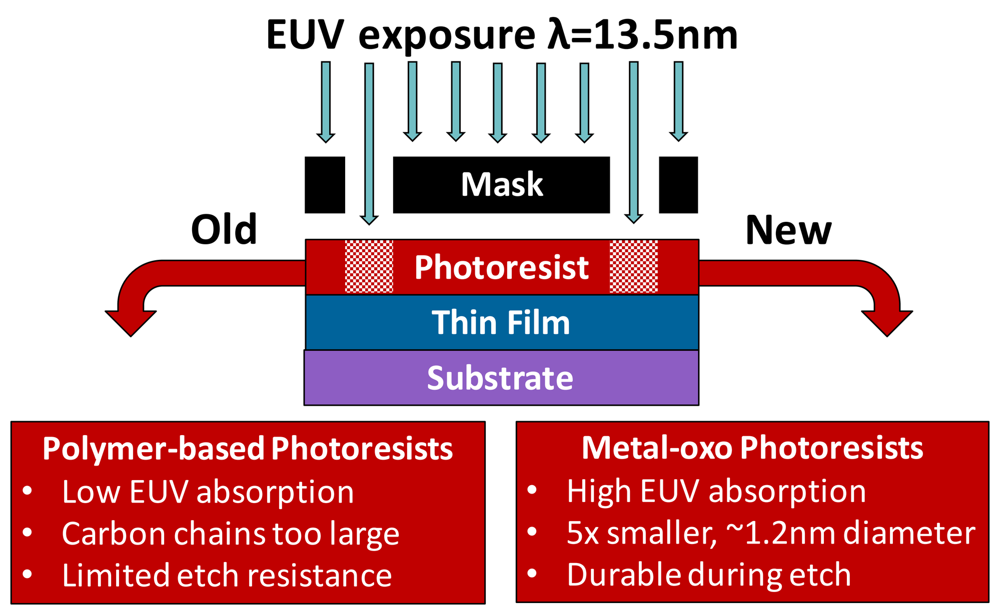
Motivation

With integrated circuit manufacturers aiming to produce sub-10nm feature sizes, extreme ultraviolet lithography (EUVL) is the next developing technology for the job. The challenges with using polymer-based photoresists for EUVL can be eliminated by using oxohydroxo metal cluster photoresists.



Previous Work on Metal-oxo Photoresists

HafSOx clusters: Demonstrated 8nm nanometer resolution, but had background condensation [1].

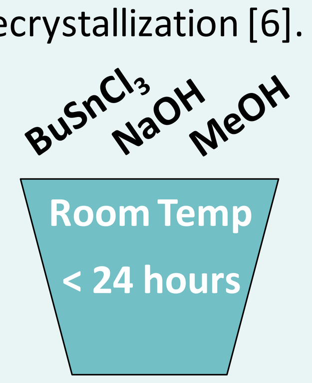
Antimony-oxo clusters: Had high EUV sensitivity, but pattern collapse limited high resolution [2].

Tin-oxo "football" cluster: Prevented background condensation, but synthesis was difficult [3].

Na-centered tin-oxo Keggin cluster: Had two recrystallization steps, but poor reproducibility and low yields [4, 5].

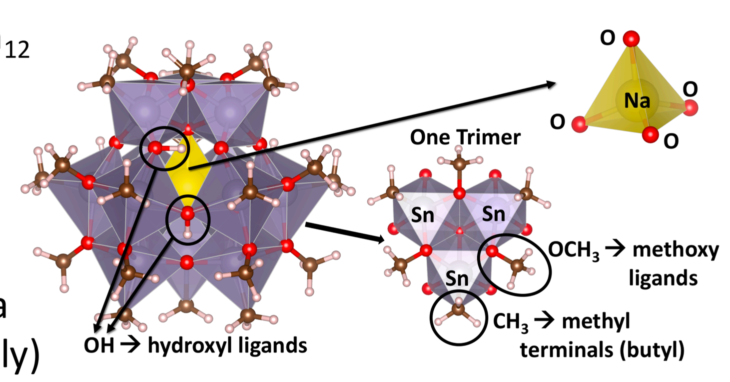
Proposed Material: $NaSn_{12}$

One-step synthesis of sodium-centered tin Keggin ion ($NaSn_{12}$) that does not require any heating, filtration, or recrystallization [6].



- Crystallized without excess counterions
- Had high yield, purity, and reproducibility
- Soluble in organic media including benzene, toluene, and 2-heptanone

- $[(BuSn)_{12}(NaO_4)O_4(OH)_8(OCH_3)_{12}]^{1+}$ deemed $NaSn_{12}$
- Central NaO_4
- Four trimer units linked by corners or edges
- Hydroxyl ligands spread throughout structure
- One trimer has 3 edge-sharing $BuSnO_5$ octahedra with methyl terminal ligands (butyl experimentally)
- Methoxy ligands at bridging oxygen within trimer
- 5 isomers obtained by 60° rotation of trimers (α, β, γ, δ, ε)



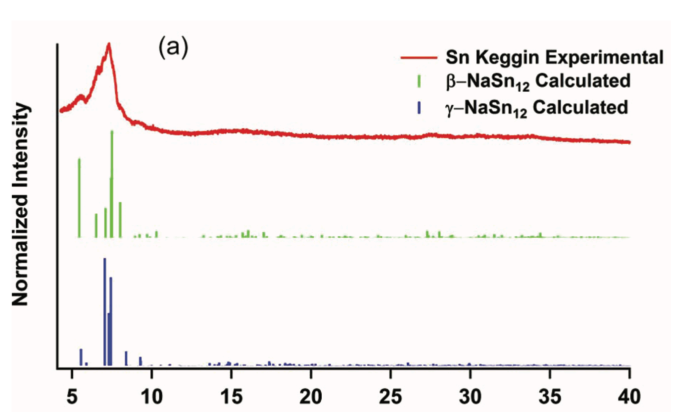


Figure 1: Experimental powder X-ray diffraction pattern for β,γ-$NaSn_{12}$ (red) with calculated powder patterns for β-$NaSn_{12}$ (green) and γ-$NaSn_{12}$ (blue).

- XRD identified mixture of β and γ isomers
- Computational studies employed to aid understanding ease of β/γ $NaSn_{12}$ isomerization

Methods

Computational Techniques

Density functional theory (DFT) was used to find the ground state electronic structure of each cluster. Solvent (water) was modeled using parameterized continuum solvation model. Hydrolysis Gibbs free energy was determined using thermodynamic cycle below.

$$12\,Sn(H_2O)_6{}^{4+}{}_{(aq)} + 6\,Na(H_2O)_6{}^{+}{}_{(aq)} + 3\,CO_{2(aq)} + 21\,CH_{4(aq)} \xrightarrow{\Delta G_{aq}} 48\,H_3O^+_{(aq)} + 8\,H_2O_{(aq)} + C_{24}H_{80}NaO_{28}Sn_{12}{}^{+}{}_{(aq)}$$

$$\downarrow -\Delta G^{solv}_{Sn(H_2O)_6^{4+}} \quad \downarrow -\Delta G^{solv}_{Na(H_2O)_6^{+}} \quad \downarrow -\Delta G^{solv}_{CO_2} \quad \downarrow -\Delta G^{solv}_{CH_4} \qquad \uparrow \Delta G^{solv}_{H_3O^+} \quad \uparrow \Delta G^{solv}_{H_2O} \quad \uparrow \Delta G^{solv}_{C_{24}H_{80}NaO_{28}Sn_{12}^{+}}$$

$$12\,Sn(H_2O)_6{}^{4+}{}_{(g)} + 6\,Na(H_2O)_6{}^{+}{}_{(g)} + 3\,CO_{2(g)} + 21\,CH_{4(g)} \xrightarrow{\Delta G_{gas}} 48\,H_3O^+_{(g)} + 8\,H_2O_{(g)} + C_{24}H_{80}NaO_{28}Sn_{12}{}^{+}{}_{(g)}$$

$$\Delta G_{aq} = \Delta G_{gas} + \sum_{i=1}^{Nproducts} n_i \Delta G_i^{solv} - \sum_{j=1}^{Nreactants} n_j \Delta G_j^{solv}$$

Hydrolysis Gibbs free energy calculated as sum of the corresponding gas-phase Gibbs free energy (ΔG_{gas}) and the Gibbs free energies of solvation (ΔG_{solv}). The ΔG_{gas} contains a correction term that takes into account the enthalpy, entropy, and temperature of the system when a frequency analysis is conducted. The term "n" is the coefficient of the species.

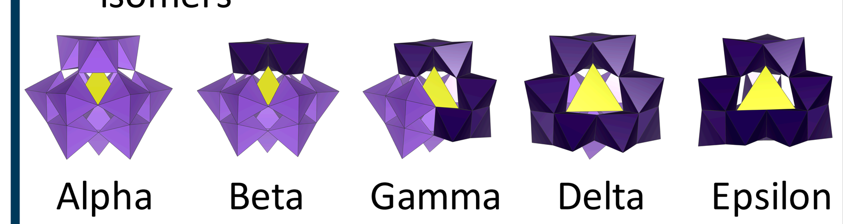
Experimental Characterization Techniques

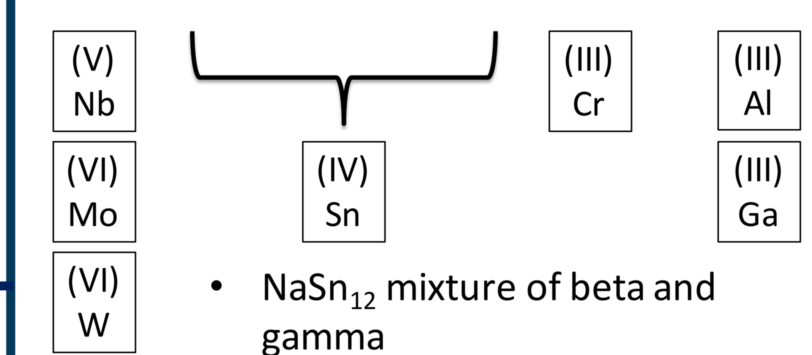
Single crystal and powder x-ray diffraction (XRD) , scanning electron microscopy (SEM), electrospray ionization mass spectrometry (ESI-MS), small angle x-ray scattering (SAXS), and proton, carbon, and tin nuclear magnetic resonance spectroscopy (NMR) performed at OSU.

Factors

Isomers

- Rotate one trimer by 60 degrees to obtain 5 total isomers
- Different metal-oxo clusters prefer certain isomers

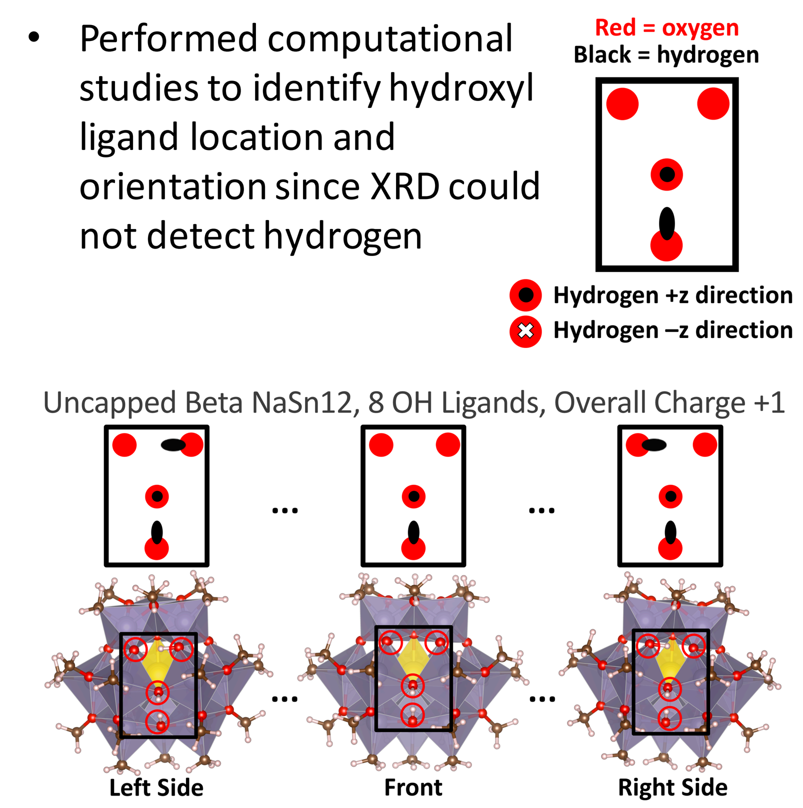




- $NaSn_{12}$ mixture of beta and gamma
- $NaSn_{12}$ system unique to prefer less symmetric isomers

Ligands

- Hydroxyl ligands assumed to be present as charge stabilizers
- Performed computational studies to identify hydroxyl ligand location and orientation since XRD could not detect hydrogen



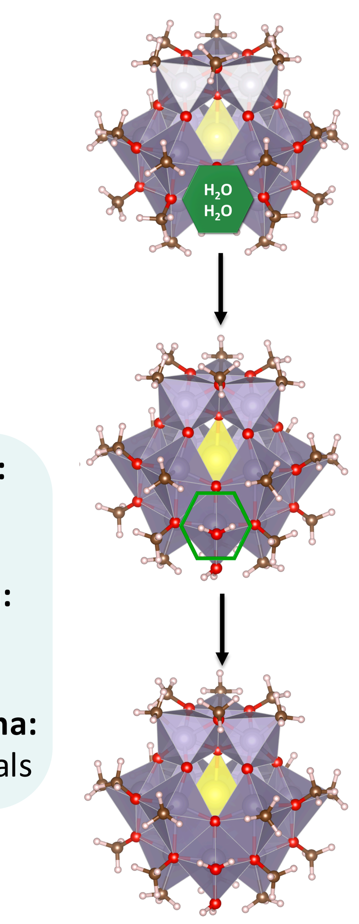
Caps

- Impure commercial precursor produced capped isomers
- A cap in this case is an extra tin atom with 2 terminal molecules

Theoretical Capped Alpha: 2 water terminals

Experimental Capped Beta: 2 water terminals

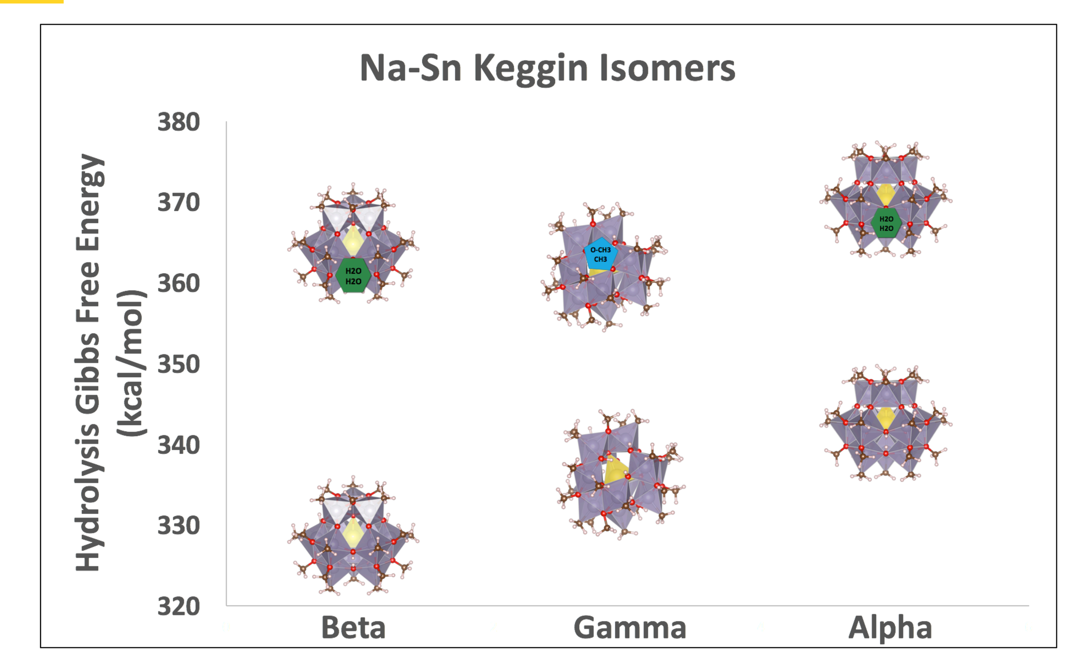
Experimental Capped Gamma: methyl and methoxy terminals



Results

- The lower the hydrolysis Gibbs free energy, the more stable the cluster
- HOMO-LUMO gap also indicator of stability: the higher the gap, the more stable the cluster

	Hydrolysis Gibbs free energy (kcal mol^{-1})	ΔG (kcal mol^{-1})	Destabilization by capping (kcal mol^{-1})	HOMO–LUMO gap (eV)
β-$NaSn_{12}$	327.4	0	—	6.24
γ-$NaSn_{12}$	337.4	10.0	—	5.91
α-$NaSn_{12}$	342.7	15.3	—	6.20
β-$NaSn_{13}$	364.9	37.5	37.5	5.28
γ-$NaSn_{13}$	361.2	33.8	23.8	5.80
α-$NaSn_{13}$	369.7	42.3	27.0	5.17



- Uncapped isomers more energetically stable than capped counterparts
- Experimental and computational results agree that the sample was a mixture of uncapped and uncapped gamma clusters
- Other EUVL studies successfully used capped beta NaSn12 as photoresist [5]

Conclusions and Future Work

- Uncapped beta and uncapped gamma show promise as EUV photoresist material
- One-step synthesis of metal-oxo cluster with limited counterions make this an excellent model system for mechanistic lithography studies
- β/γ for Sn(IV) provides balance between cation-cation repulsion (corner-linking) and stability via bond formation (edge-linking)

1. Change central heteroatom (K, Mg, Ca) to determine how stability is affected
2. Elucidate importance of ligands by examining other metal-oxo clusters like Hf, Zr, and Fe to guide synthesis procedures and aid tuning ligands to best influence solubility switch upon EUV exposure
3. Explore other solvation models and solvents to identify environmental effect on stability

Acknowledgements

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