Effect of Ambient Conditions on Radiation-Induced Chemistries of a Nanocluster Organotin Photoresist for Next-Generation EUV Nanolithography

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Supporting Information

Zr M_ζ Anode XPS

To confirm that the β-$NaSn_{13}$ photoresists also undergo the insolubility transition with soft X-rays we have used Zr M_ζ radiation (hv = 151.4 eV, 75W, 15kV) as the radiation source to make a contrast curve for exposures in UHV. An XPS full survey using Zr M_ζ X-rays was collected over a wide kinetic energy (KE) range including the secondary electron peak, shown in Figure S1. The large secondary electron peak at low KE (~10 eV) displays the importance of these electrons in the resulting chemistry due to the extreme number of electrons generated. An electron analyzer pass energy of 30 eV and normal emission was used for this data. The survey was collected with the source retracted 5 mm to lower the intensity and prevent saturation of the detector due to the secondary electron peak. High resolution spectra were collected with a pass energy of 30 eV, 40° emission angle, and fully extended source positioned directly in front of the sample. The high-resolution

spectra were fit using Gaussian-Lorentzian line shapes and a linear background. Two distinguishable peaks were detected corresponding to Sn 4d and O 2s at 120.4 eV and 124.2 eV KE (31 eV and 27.2 eV binding energies), respectively.

A contrast curve using Zr M_ζ radiation is shown in Figure S2. The dual anode source results in X-ray exposures over the entire sample surface, therefore multiple samples were used to collect a contrast curve. Monochromated Al Kα XPS was used in three fresh spots to obtain C 1s, O 1s, and Sn 3d spectra. The collection of AP-XPS was also used to verify each sample was the same since multiple samples were required for these experiments. Following each exposure, the sample was removed from vacuum and immediately developed. Ellipsometry was collected for each sample in the same method as described previously in experimental. Spots that were exposed with Al Kα radiation were visible and ellipsometry was avoided in these areas. A clear and distinct “S” curve occurs for the Zr M_ζ, similar to the Al Kα curves in Figure 1. After 1500 seconds of Zr M_ζ X-ray exposure a solubility transition occurs. This suggests that lower energy photons, close to the energy of EUV, can induce similar chemistry to that of Al Kα X-rays.

A Sn 3d spectrum was collected with each experiment in addition to the C 1s and O 1s spectra shown in the manuscript. No distinct changes were seen in the Sn 3d spectra suggesting that the oxidation state does not change. Reactions for the tin are possible through interactions with other species in the film, which allows the oxidation state to remain the same. Prior studies have shown no change in the binding energy following a photon dose sufficient enough to change the resist solubility [Frederick et al., *ACS Appl. Mater. Interfaces*, 2019, 11, p. 4514]. These studies also used X-ray induced Auger spectra to calculate an Auger parameter for these resists, both before and after exposure, suggesting that Sn^{4+} was the dominant oxidation state.

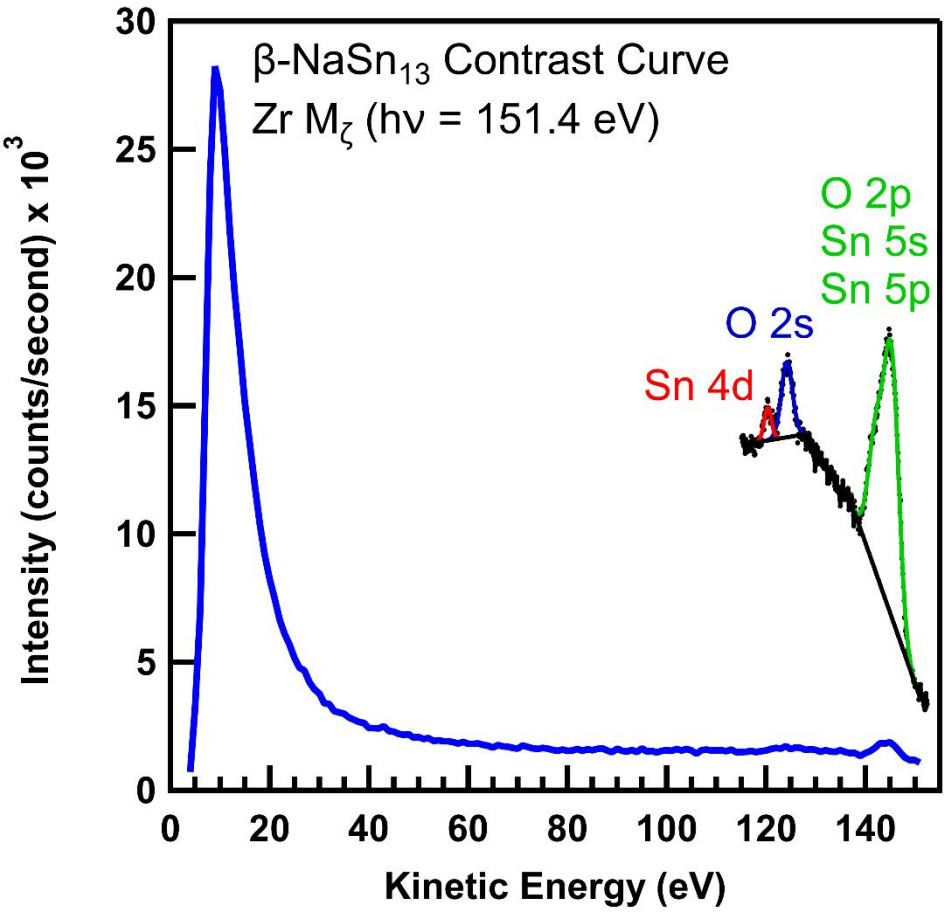

Figure S1. Photoemission survey with Zr M_ζ X-rays capturing the secondary electron peak in the low kinetic energy (0-20 eV) regime. Zooming into the 115- 150 eV KE range we can see resolved Sn 4d (red) and O 2s (blue) photoemission peaks as well as the valence band.

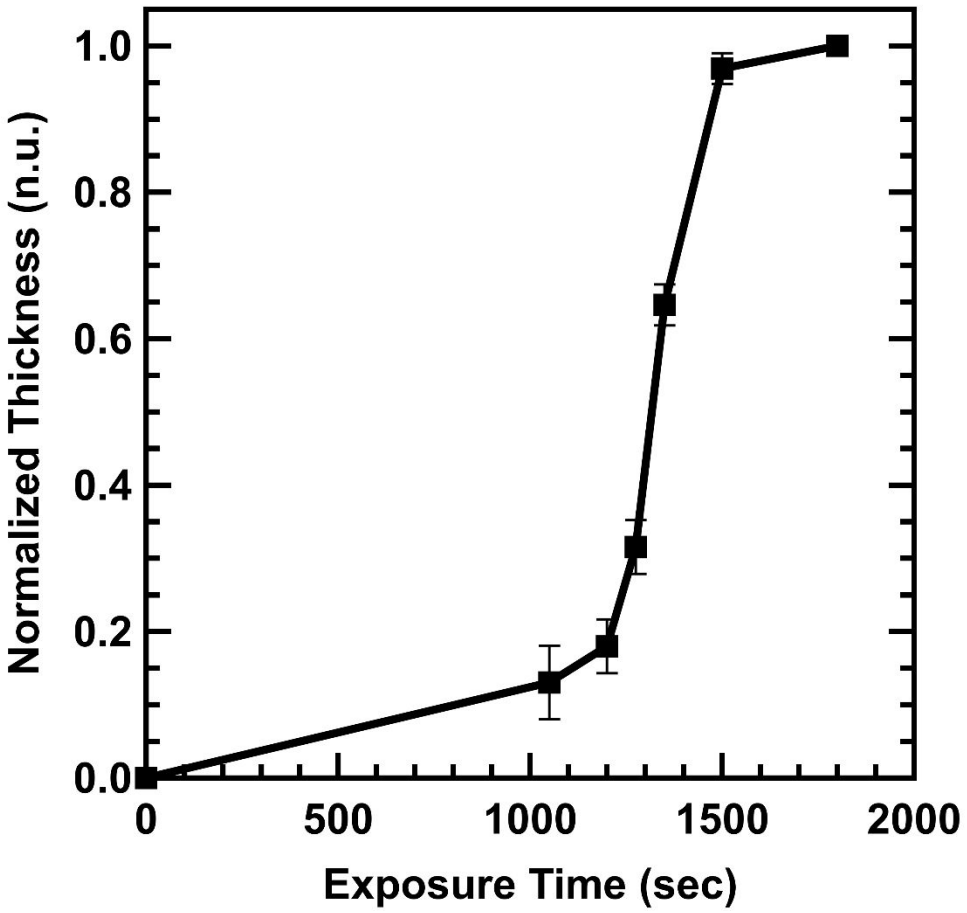

Figure S2. β-$NaSn_{13}$ contrast curve of using Zr M_ζ X-rays (75 W, 15 kV, 80° impingement).

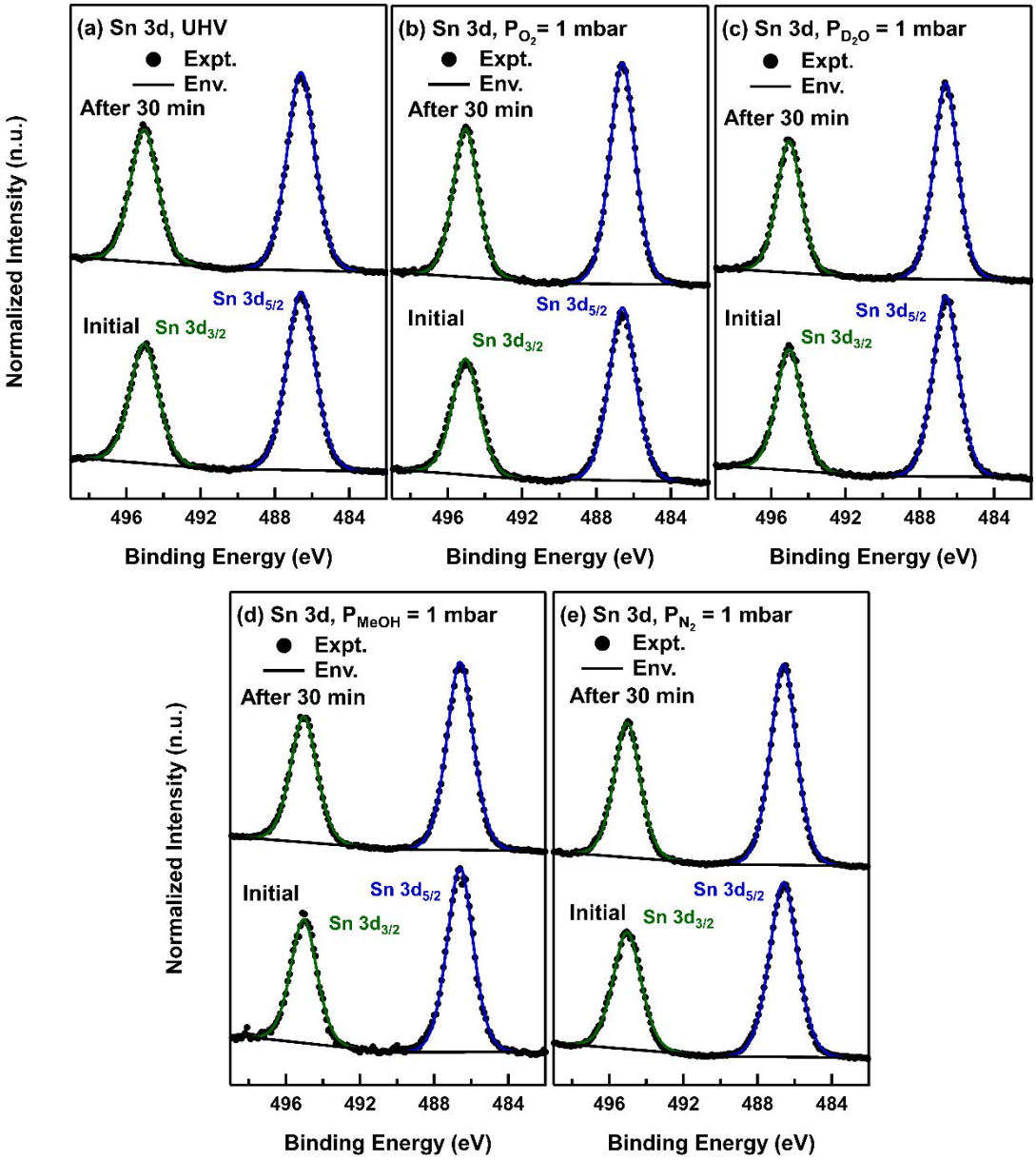

Figure S3. XPS for Sn 3d during exposure: (a) to UHV, (b) P_{O_2}= 1 mbar, (c) P_{D_2O} = 1 mbar, (d) P_{MeOH} = 1 mbar, and (e) P_{N_2}= 1 mbar for both before X-ray exposure (initial) and after 30 min of exposure.