



Role of Low-Energy Electrons in All-Dry Processing Strategies for Semiconductor Technologies

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The continued scaling of semiconductor devices is driving the development of all-dry processing strategies that eliminate solvent-based development and wet chemical etching while providing increasingly precise control over material transformation at the nanoscale. In this presentation, I will describe two recently developed all-dry approaches that are dependent on low-energy electron-mediated chemistry: vapor-phase development of inorganic EUV resists and resist-free patterning of two-dimensional transition metal dichalcogenides (TMDs).

(i) All-Dry Zinc-Imidazolate Resists for Electron-Beam and EUV Lithography.

Amorphous zinc-imidazolate (aZnMIm) thin films are promising materials for next-generation high-numerical-aperture EUV lithography because they can be deposited by atomic/molecular layer deposition (ALD/MLD) as sub-20 nm films with angstrom-level roughness and without solution processing. We demonstrate that aZnMIm, previously established as a high-resolution electron-beam resist, also functions as a negative-tone EUV resist that can be developed entirely in the vapor phase using 1,1,1,5,5,5-hexafluoroacetylacetone (hfacH).¹ EUV exposure predominantly produces H₂, while chemical analysis indicates that resist conversion involves densification and structural degradation of the imidazolate without significant changes in the Zn:C:N ratio. Subsequent hfacH development selectively removes unexposed material, enabling an all-dry resist process without liquid developers or solvent waste. Low-energy electrons are proposed to mediate the localized chemical transformations that render exposed aZnMIm resistant to hfacH. EUV photoelectron spectroscopy, reflectometry, total electron yield, residual gas analysis, and time-of-flight secondary ion mass spectrometry were used to examine the relationship between EUV irradiation, electron emission, and resist conversion. aZnMIm exhibits substantially greater primary and secondary electron emission than poly(4-hydroxystyrene), while producing a smaller fraction of low-energy electrons relative to the primary electron population.²

(ii) Dry Patterning of Transition Metal Dichalcogenides by Photooxidation.

The spatial control of two-dimensional TMDs is critical for their integration into semiconductor devices. Although substrate engineering and seeding strategies can improve the growth and orientation of CVD-grown TMDs, they do not provide the post-synthetic spatial selectivity needed for device fabrication. To address this challenge we have developed a plasma-free and resist-free dry patterning strategy based on photon-induced electron chemistry, in which UV irradiation generates low energy secondary electrons that convert WS₂ into WO₃ in exposed regions. This chemical contrast is subsequently translated into a physical pattern through selective gas-phase etching. Treatment with WCl₆ converts the WO₃ regions into volatile tungsten oxychloride species at temperatures below 200 °C, while the parent WS₂ remains unaffected.

