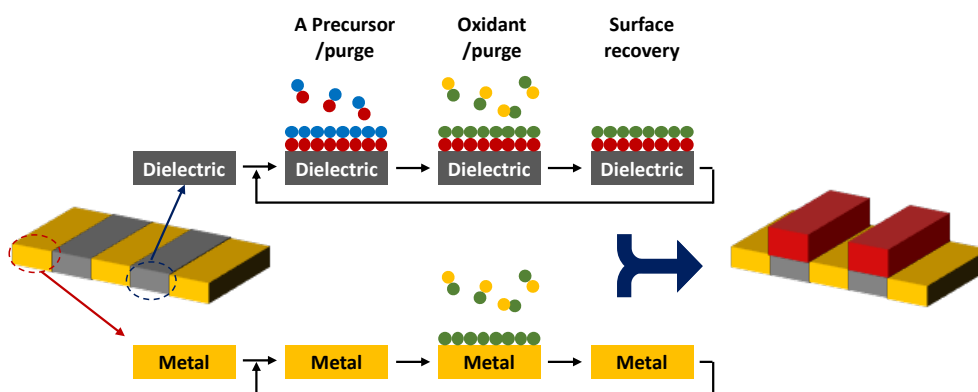


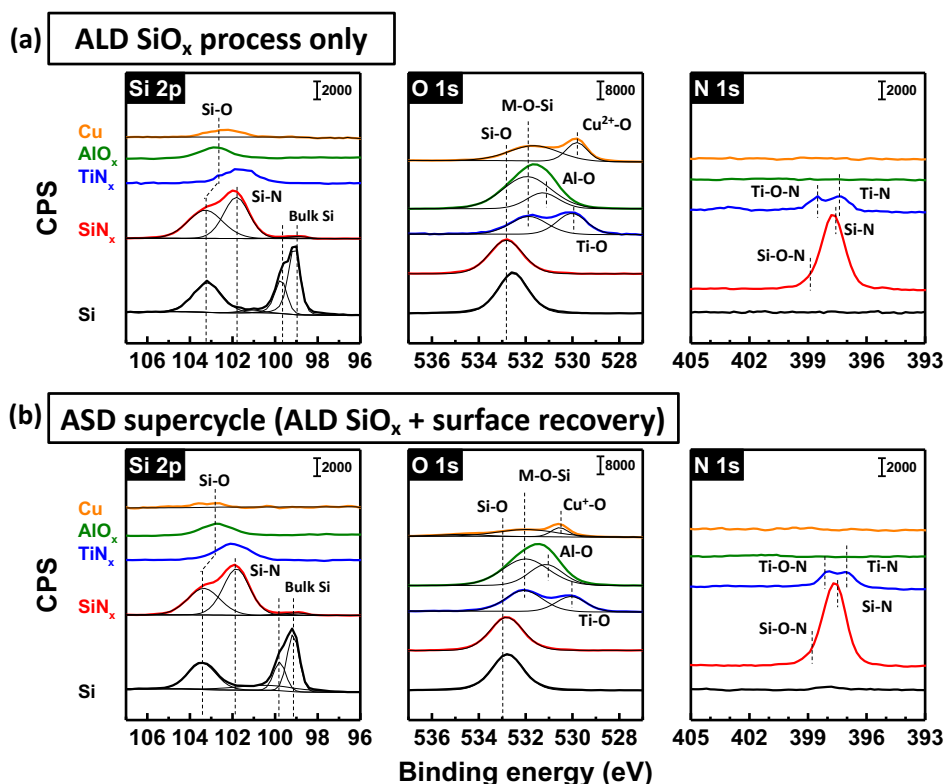
(Supplemental)

## In-situ Surface Cleaning and Area Selective Deposition of $\text{SiO}_x\text{N}_y$ film on Cu using Anhydrous $\text{N}_2\text{H}_4$

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**Figure 1.** Schematic illustration of ideal AS-ALD of dielectric-on-dielectric patterns using ABC-type ALD cycle with surface cleaning agent. ‘A’ precursor can be only adsorbed in the dielectric area, whereas co-reactant (‘B’ precursor) can oxidize both of adsorbed precursor and the clean metal surface. Subsequently, with the introduction of  $\text{N}_2\text{H}_4$  (‘C’ pureursor), the oxidized metal surface (can be recovered to the initial metallic surface without changing the surface condition of the dielectric area.



**Figure 2.** XPS spectra of Si 2p, O 1s, and O 1s on different substrates after 5 cycles of (a) ALD  $\text{SiO}_x$  only and (b) ABC-type ALD of  $\text{SiO}_x$ . With five supercycle ALD- $\text{SiO}_x$  processes, the unchanged growth of  $\text{SiO}_2$  on both bare Si and  $\text{SiN}_x$  substrates, formation of metal-silicates (and/or  $\text{SiO}_x$ ) on  $\text{TiN}_x$  and  $\text{AlO}_x$  suggest that the supercycle-based ALD- $\text{SiO}_x$  process does not impact the growth of  $\text{SiO}_x$  on top of dielectric substrates. On the other hand, the deposited amount of  $\text{SiO}_x$  on Cu substrate is approximately 35% less than the previous ALD- $\text{SiO}_x$  process. Furthermore, the formation of  $\text{Cu}_2\text{O}$  (530.4 eV) rather than  $\text{CuO}$  (529.6 eV) suggests that  $\text{N}_2\text{H}_4$  slightly inhibited the oxidation of the Cu surface. In N 1s narrow scan, nitridation of the Cu surface by  $\text{N}_2\text{H}_4$  is not observed, indicating that most of the introduced  $\text{N}_2\text{H}_4$  molecules were used to reduce surface oxide without any formation of Cu-N bond.