(Supplemental)

Effect of copper surface condition on passivation characteristics for applications to area selective atomic layer deposition

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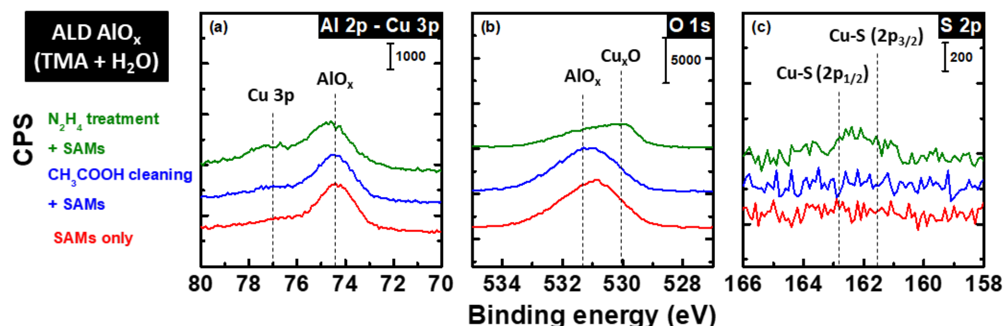

Figure 1. *Ex-situ* XPS results following ALD–AlO_x process of different Cu samples at 120 ºC showing (a) Al 2p–Cu 3p, (b) O 1s, and (c) S 2p narrow scans. In case of passivated as-is Cu (red) and passivation after CH_3COOH cleaning (blue), AlO_x was detected, whereas peak corresponding to Cu-S bonds were not detected. It implies that the Cu surfaces were passivation with poor adhesion, resulting in relatively low selectivity of ALD-AlOx. On the other hand, N_2H_4 treated Cu (green) gives better SAMs stability as well as less formation of AlO_x.

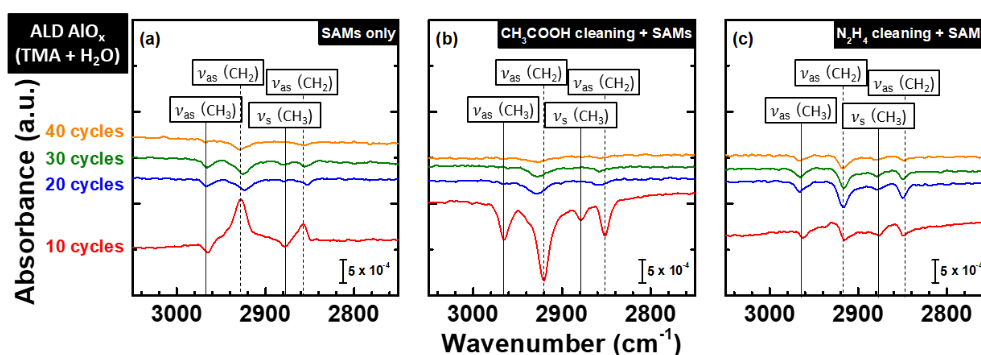

Figure 2. Differential IR spectra of the stability of SAMs-Cu samples against ALD–AlO_x process at 120 ºC. (a) In the case of passivated as-is Cu, positive peaks of (-CH_2) were only observed, indicating reorientation of SAMs parallel to the substrate. (b) On the other hand, the SAMs on the CH_3COOH-treated Cu sample were desorbed within ten cycles of the ALD process.

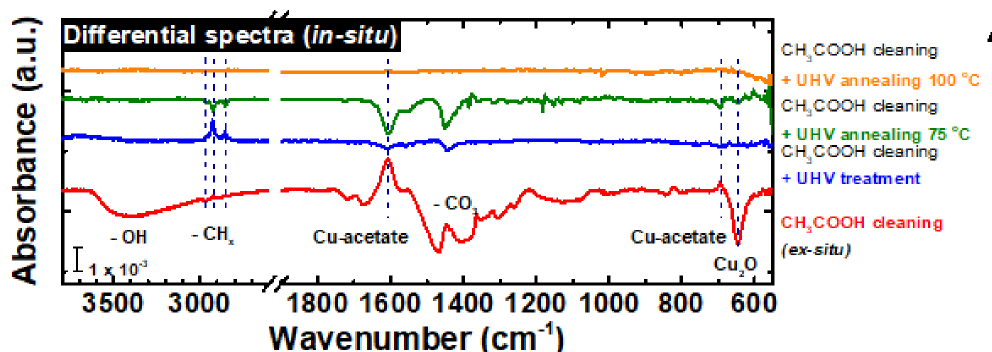

Figure 3. Differential IR spectrum of four different surface treatments on the Cu substrate. The *ex-situ* CH_3COOH cleaning process (red) shows removals of surface contaminants(e.g., –CH_x, –OH and –CO_3), reduction of Cu_2O, and formation of the copper acetate. Under the vacuum treatment (blue, ~10^{-8} Torr), the copper acetate can be partially reduced to –CH_x and –OH species. Most importantly, consecutive annealing process at 75 ºC (green) can effectively modify the surface condition by removing residuals as well as the copper acetate.