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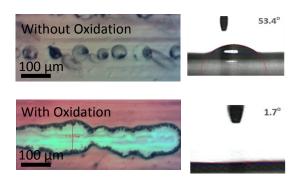
PAPER



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Supplementary Fig. S1



XRD analysis

According to XRD spectrum, the printed Al₂O₃ XRD peaks show the $\gamma - Al_2O_3$ phase at 47.48°, which indicated $\gamma - Al_2O_3$ phases present before annealing process (Figure 2(a) green line, and Figure 2(b)).

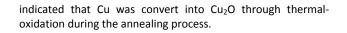
For the free flow condition as annealing with H_2 only, without spacer and cap situation, Al_2O_3 barriers were etched away (Figure (c)), and XRD peaks only present Cu crystal peaks at 43.28°, 50.40°, corresponding to (111), (200), respectively (JCPDS Copper: 04-0836)(Figure 2 blue line).

Under the annealing with Ar condition (Figure 2(a), black line and Figure 2 (d)) was to mimic the Al₂O₃ barriers annealing process with the cap and spacer condition, which is to consider the limited H₂ gas flow during the annealing process. As the Figure 2 black line and Figure (d) shown the $\alpha - Al_2O_3$ present after annealed with Ar only, which may imply that the $\gamma - Al_2O_3$ can be preserved without H₂ etching and convert into a stable $\alpha - Al_2O_3$ in the real condition.

Notice that Cu₂O (111), (200) (JCPDS card, no# 125678-2076) (Figure 2 blue line) phase appeared after annealing wit Ar only process, and no strong Cu (111) and (200) present, which

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