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Ultra-Conformal Metal Coating on High-aspect-ratio 3D Structures using Supercritical Fluid: Controlled Selectivity/Non-Selectivity

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We have successfully coated Cu conformally on high-aspect-ratio trenches (aspect ratio 50) with SiO_2 surface using supercritical fluid deposition (SCFD). The SCFD, which has a remarkable potential for ultra-conformal deposition and gap-filling, has required metallic underlayer similarly with electroplating, but we have overcome this constraint by introducing a novel glue layer, $CuMnO_x$. This breakthrough extended the applicability of this process to numerous MEMS applications such as a wiring in 3D chip integration, a high-aspect ratio electrode in glass-based MEMS, and even flexible MEMS using polymers.

The SCFD of metals, which is a chemical reduction of metal-organic compounds with H_2 in supercritical CO_2, is a strong tool for functional coating on fine 3D structures [1,2]. Conformal deposition and gap-filling onto high-aspect-ratio vias covered with metal underlayer has been demonstrated (**Fig. 1**) [2]. In SCFD, metal films could be selectively deposited on conductive underlayers because the reducing agent, H_2, is only activated on metallic surfaces.

On the other hand, metal coating on Si 3D structure is widely used. There is also an increasing demand for metal filling onto the high-aspect-ratio (>100) vias with insulating surface for applications such as wiring in 3D packaging, coating on the inner surface of fluid channels, and electrode contacts to the channels in micro-fluidic chips. Therefore, novel SCFD technique which realizes metal coating on Si and/or insulative substrate will be a strong tool for MEMS fabrication. In order to control the selectivity/non-selectivity of the SCFD of metals, we need a surface pretreatment which promotes initial growth of metal SCFD on such surfaces, or a glue layer between an insulating substrate and a metal film which also works as a catalytic layer of metal SCFD.

Conformal Cu coating on Si surface: With the SCFD, it is impossible to deposit Cu film on the surface of Si trenches prepared by a conventional Bosch process (**Fig. 2**). By removing the native surface oxide layer and terminating the surface by H atoms with HF wet treatment, we successfully coated highly-conformal Cu film on the trench with the aspect ratio of 50 (**Fig. 3**).

Conformal Cu coating on silicon oxide surface: Figure 4 shows that the SCFD of Cu does not occur on a SiO_2 surface. Deposition of oxide films, in contrast, is known to exhibit no dependence on underlayers. If there is a material that exhibits the natures of oxides and metals at the same time, it can function as a glue layer between an oxide underlayer and a metal film. This material, as we have successfully found, is $CuMnO_x$ [3].

The SCFD of the $CuMnO_x$ glue layer is made possible by the simultaneous supply of Cu and Mn precursors, and H_2. At the initial nucleation on the SiO_2 surface, MnO_x is deposited on the SiO_2, and then Cu can be co-deposited with MnO_x probably by a catalytic effect of MnO_x. The $CuMnO_x$ layer deposited in this way functions as a catalytic underlayer for the reductive deposition of Cu with H_2 (**Fig. 5**). For the $CuMnO_x$ layer to serve both as an adhesive and a catalyst for Cu deposition, the stoichiometry of $CuMnO_x$ is vital to strike a balance between metal and oxide. By optimizing the chemistry, $CuMnO_x$ film was conformally formed on Si trenches with SiO_2 surface and Cu was conformally deposited as shown in **Fig. 6**. Since the gap-filling of Cu using a metallic underlayer was already established, Cu filling onto high-aspect-ratio trenches with an insulating surface is achievable.

The $CuMnO_x$ glue layer is also applicable for the deposition of other metals such as Au and Ru on insulating surfaces, allowing us to explore new frontier for MEMS fabrication.

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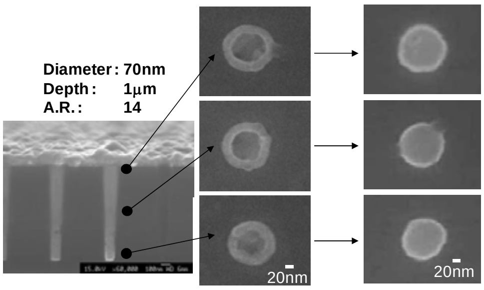

Figure 1. Left and right columns: Via holes filled with Cu by SCFD. The surface of vias was coated with metallic Ru by an atomic layer deposition method prior to the SCFD of Cu. The left picture is the cross sectional SEM image and the pictures in the right column are plain-view SEM images after angled polishing, confirming complete filling with Cu. The pictures in the center column are for the trenches with 10-nm-thick conformal Cu film by SCFD.

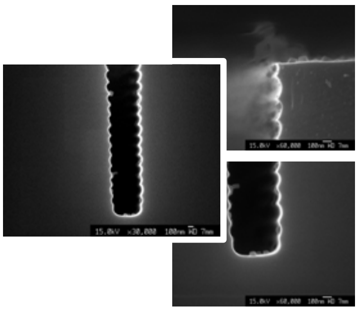

Figure 2. Cross-sectional SEM images of Si trenches after the SCFD of Cu without surface treatment. No Cu film is found on the surface.

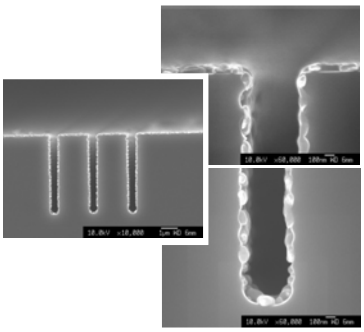

Figure 3. Cross-sectional SEM images of Si trenches after the SCFD of Cu with 5% HF treatment for 1 min prior to Cu-SCFD. Conformal Cu film is successfully deposited on the surface.

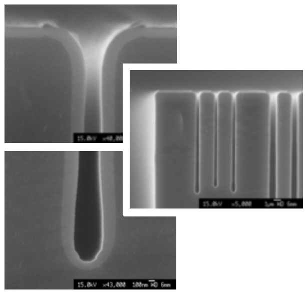

Figure 4. Cross-sectional SEM images of Si trenches with thermal SiO_2 on the surface after the SCFD of Cu. No Cu film is found on the surface.

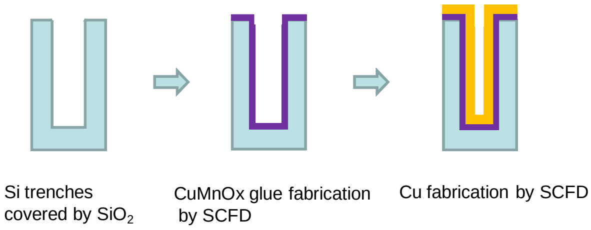

Figure 5. Process flow of the Cu-SCFD onto an insulative surface. $CuMnO_x$ film was firstly deposited by SCFD, and Cu was formed on $CuMnO_x$ by SCFD. The $CuMnO_x$ film has the characteristics of both an insulator and a metal.

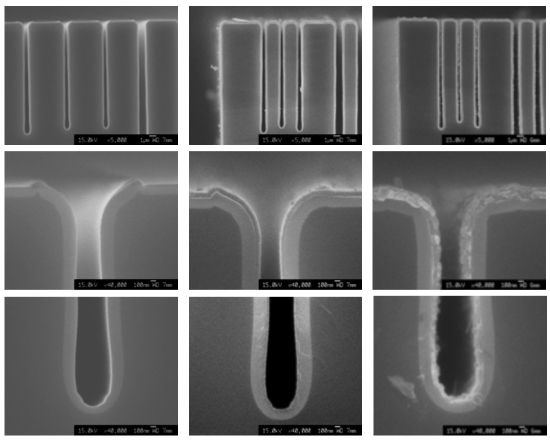

Figure 6. Cross-sectional SEM images of Si trenches with thermal SiO_2 on the surface. Left column: before any deposition. Center column: after the SCFD of $CuMnO_x$. Right column: after the SCFD of Cu. Conformal Cu film is successfully deposited on the oxide surface.

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