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Fabrication of Freestanding Metallic Micro Hollow Tubes by Template-Free Localized Electrochemical Deposition

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We describe a technique to fabricate three-dimensional (3D), freestanding metallic micro hollow tubes by template-free localized electrochemical deposition. The features of the grown structure are controlled by the field strength distribution in its proximity that depends on the applied voltage and the microelectrode-structure distance (L). The formation of micro hollow tubes is induced by the enhanced electric field at the microelectrode rim for small L values (a few micrometers or less) and high applied voltages.
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A strategy is presented to fabricate three-dimensional (3D), freestanding micro hollow tubes by localized electrochemical deposition (LECD).[1-5] The strategy is based on accurately controlling the distribution of the electric field strength during deposition with a precise interplay of the applied voltage and the distance L between the microelectrode and the grown structure.

The fabrication of microdevices is a fundamental issue in modern technology.[6] Diverse techniques were developed to fabricate microstructures consisting of semiconductors, metals, and polymers.[7-10] Freestanding, three-dimensional (3D) hollow tubes are particularly promising for broad applications in diverse areas such as optics,[11] electronics,[12] medical technology,[13] and microelectromechanics.[14] Such structures are typically fabricated by conventional lithographic processes such as LIGA,[7] the track-etch method,[15] or laser-assisted chemical vapor deposition (LCVD).[16] Among these techniques, LIGA, using synchrotron X-rays, was the most useful technique. Even this process, however, is affected by significant problems: it implies multiple fabrication steps, long fabrication times, and high cost due to the use of sophisticated masks or molds. Furthermore, the electroplating solution cannot easily fill high-aspect-ratio trenches. In general, using LIGA it is difficult to produce complex 3D structures.

We developed an alternate approach based on LECD with significant advantages with respect to LIGA. Specifically, it is a simple, inexpensive, and damage-free method without any damage-inducing steps such as beam irradiation, chemical etching, and development.

The LECD approach is based on electrochemical deposition: the microelectrode (anode) is placed very close to the conducting substrate (cathode) immersed in the plating bath.[8] As the voltage is applied and the microelectrode is moved up, a metallic microstructure is fabricated that protrudes toward the microelectrode. The process is thus particularly suitable for producing high-aspect-ratio metallic structures with a variety of features. This simple approach can be applied to different materials such as metals, metal alloys, conducting polymers, and semiconductors to fabricate objects in the micrometer, sub-micrometer, and nanometer scale.

In this paper, we have studied the effect of the microelectrode-structure distance (L) on the shape and the density of the electroplated copper structure. Noticing that the hollow tube was obtained in small L value, we have optimized the experimental conditions [i.e., distance (L) and electric field strength] to produce dense and regular copper hollow tubes.

We conducted tests at room temperature using 1.05 M $CuSO_4{\cdot}5H_2O$, 0.8 M H_2SO_4. The microelectrode with 50 μm diameter was prepared by sealing Pt wire (99.95%, Alfa Aesar) in a glass tube and then polishing the surface. Platinum-coated silicon wafers were used as cathodes. The microelectrode position was accurately controlled by three stepping motors. The experiments were performed at the "7B2 X-ray Microscopy" beamline of the Pohang Light Source (PLS), Korea.[17] Additional tests such as field emission scanning electron microscopy (FE-SEM, JEOL JSM6330F) were used to study the microscopic characteristics of the grown structures. For the FE-SEM image, the electroplated sample was cleaned using deionized (DI) water. The microradiographic monitoring of the LECD process was implemented in situ in a specially designed miniature electrochemical cell machined from a Teflon block and sealed by Kapton films that were X-ray transparent and stable for most chemical reactions. The distance between the two cell windows was optimized to ~5 mm to avoid unnecessary X-ray absorption by the plating electrolyte. For microtomography,[18] the grown structure was mounted on a translation/rotation stage with precise positioning (250 nm/0.002°), and 1000 projection radiographs were taken while rotating the sample between 0 and 180°. Slice images were then reconstructed by using a self-developed reconstruction algorithm.

Figure 1 shows FE-SEM images of a 3D copper wire fabricated by the LECD process with an applied voltage of 4.5 V. Figure 1a reveals two growth regimes: the upper part (shown in detail in Fig.

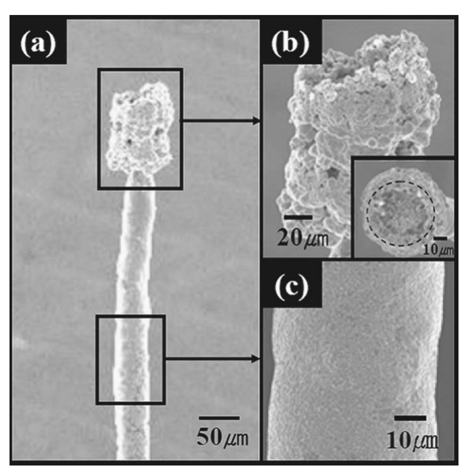

Figure 1. FE-SEM images of a 3D copper wire fabricated with an applied voltage of 4.5 V with an electroplating solution of 1.05 M $CuSO_4{\cdot}5H_2O$, 0.8 M H_2SO_4. In (a) we see an overall picture of the wire revealing two different growth regimes, illustrated in detail in (b) and (c). Specifically, (c) is the dense growth obtained for $L \approx 40$ μm and (b) the porous one produced when L is reduced to a few micrometers. The top view in the inset of Fig. 1b reveals a hollow-shaped feature with diameter not far from the 50 μm value of the microelectrode (dashed circle).

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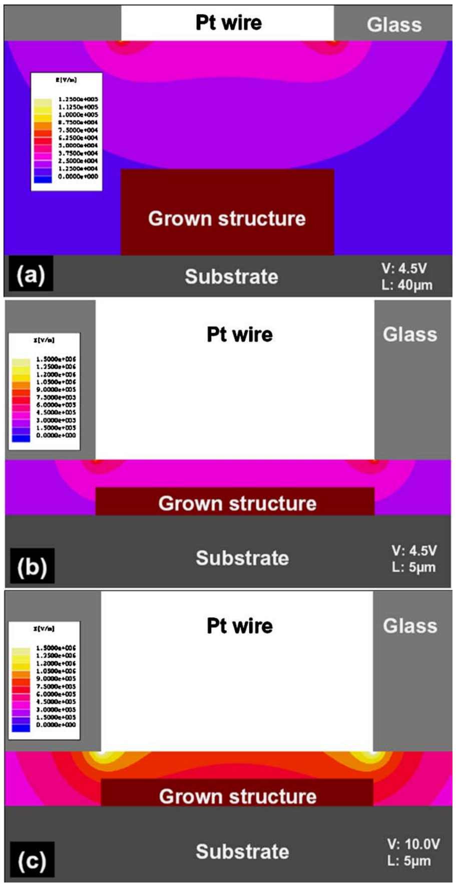

Figure 2. (Color online) Distribution map of the electric field strength for different values of the applied voltage V and of the distance L: (a) $V = 4.5$ V and $L = 40$ μm; (b) $V = 4.5$ V and $L = 5$ μm; (c) $V = 10.0$ V and $L = 5$ μm.

1b) corresponds to a regime yielding a porous microstructure, whereas the other regime results in a dense uniform microstructure (Fig. 1c). The dense uniform growth was obtained with a relatively large distance between the microelectrode and the growing structure, $L = 40$ μm (no-contact growth mode).[2] The dense, uniform growth abruptly changed to a porous growth when L was reduced to a few micrometers (contact growth mode).[2]

In order to understand this change in the growth characteristics, we must consider the mass-transport mechanisms of metal ions. Diffusion of metal ions from the bulk solution to the cathode dominates conventional electrochemical deposition.[19] In LECD, however, we must take into account the migration of metal ions that is driven by strong, localized electric fields. The distance L determines the interplay between diffusion and migration.[3] Specifically, diffusion prevails at large L values, whereas migration increasingly dominates as L decreases. When L reaches the critical value at which migration replaces diffusion as the dominating factor, the deposition rate rapidly increases because of the strong electric field,[2,3] changing the grown structure from dense to porous, as seen in Fig. 1. The top view shown in the inset of Fig. 1b reveals a hollow feature within the porous wire; the diameter of this feature is not far from that of the microelectrode (dashed line).

The electric field strength distribution near the grown feature thus has a strong influence on the growth characteristics. We modeled this distribution and the results are illustrated in Fig. 2. For a low applied voltage of 4.5 V and a large L distance of 40 μm, the electric field strength exhibits a maximum value at the center of the grown feature (Fig. 2a). We expect, therefore, the formation of a wire with a cone on top. As L decreases to 5 μm, a value much

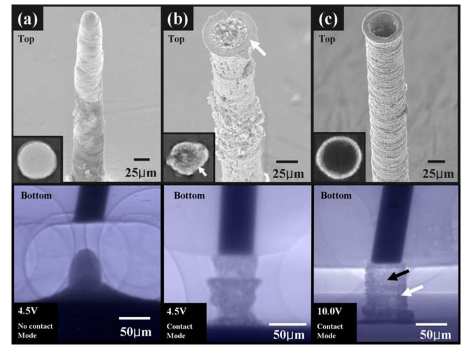

Figure 3. (Color online) LECD growth of well-defined hollow tube. Top: FE-SEM images and (inset) tomographic slices of the grown structures. Bottom: real-time images of the LECD process by coherent X-ray microradiography. The images show (a) a dense wire obtained at 4.5 V in the no-contact growth mode; (b) a porous wire obtained at 4.5 V in the contact growth mode; and (c) a well-defined hollow tube obtained at 10.0 V, again in the contact growth mode. The contrast difference in (c) between the inner (black arrow) and outer (white arrow) regions in the radiographic image reveals the formation of a hollow tube.

lower than the critical level (Fig. 2b), the maximum field position moves to the edge of the grown structure just below the rim of the microelectrode. Thus, the formation of the porous region with the hollow feature of Fig. 1b can be explained by the electric field edge enhancement at the microelectrode rim that induces a high migration rate below the rim.

As the applied voltage increases from 4.5 to 10 V for $L = 5$ μm, the electric field strength sharply increases at the microelectrode rim, enhancing the field strength difference with respect to the microelectrode core (see Fig. 2b and c). Consequently, the electrochemical deposition is also enhanced below the rim. The consistent results of the field simulation and of the actual growth thus suggest that it is possible to change the copper-grown structure from a dense wire to a well-defined hollow shape simply by controlling the electric field distribution near the microelectrode.

This analysis led us to the new strategy to fabricate well-defined hollow tubes, a strategy based on the control of the electric field strength near the grown structure, as suggested by Fig. 2. As the applied voltage is increased in the contact growth mode (the migration dominant regime), the growth enhancement below the microelectrode rim eventually produces a tube rather than a wire.

Figure 3 illustrates a result of this approach for copper-grown structures on Pt substrates. The top and bottom parts show FE-SEM images and microradiographic images obtained by real-time coherent X-ray imaging,[18,20,21] respectively. A dense wire is produced at 4.5 V by the no-contact growth mode (Fig. 3a). The tomographic slice reconstruction in the inset of Fig. 3a shows that the wire is not only dense but also uniform. The cone shape on top of the wire is the result of the field-induced local migration discussed above (see Fig. 2a). The oxygen bubbles generated on the microelectrode have no noticeable effect on the growth of the deposit, mostly escaping from the microelectrode-structure gap due to buoyancy as their size increases.

A porous structure is obtained at 4.5 V in the contact growth mode, as illustrated in Fig. 3b, but a dense rim feature is present around the porous structure (white arrow), as confirmed by the X-ray tomographic slice in the inset of Fig. 3b (top). As the applied voltage is increased to 10 V, the grown structure changes again, becoming a well-defined hollow tube with a very uniform wall thickness (~5 μm), as shown by the FE-SEM image of Fig. 3c (top) and by the corresponding tomographic slice in the inset. This is the limit result of the migration enhancement near the rim produced by a highly confined, strong electric field. The coherent X-ray microimages of Fig. 3c (bottom) illustrate this process in real time.

In conclusion, we demonstrated that a careful manipulation of the electric field strength distribution and in general of the growth parameters, enables LECD to fabricate well-defined metallic micro hollow tubes. These results were made possible by a careful control of the interplay between migration and diffusion, in turn determined by the field strength. The practical cases discussed here are only a few examples of the broad variety of metal structures that our novel LECD approach can produce by appropriate tuning of the growth parameters.

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