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Improved Copper Microcolumn Fabricated by Localized Electrochemical Deposition

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Surface quality, geometry confinement, internal integrity, and mechanical properties are of great importance for the applications of microstructures fabricated by localized electrochemical deposition. This study shows that the copper microcolumn grown by resuming the anode and cathode to a given separation when the short-circuit contact occurs exhibits a nodular structure with microvoids residing on the nodular boundaries. Both the nodular structure and voids affect the apparent Young's modulus of the microcolumn. A deposition-detection-withdrawal control method, which totally avoids the short-circuit contact, is thus developed to grow the microcolumn with improved geometry confinement and internal integrity.
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Interest in fabricating microstructures and nanostructures has led to the development of several nonconventional fabrication techniques such as lithographie, galvanoformung, abformung (LIGA)[1,2] and localized electrochemical deposition (LECD),[3,4] etc. The basic difference between these two techniques is that the microstructure is made via electrodeposition on substrates with and without patterns for LIGA and LECD, respectively. Consequently, the LECD process is generally less expensive than the LIGA process.[5-7] Furthermore, LECD avoids the difficulty in filling the solution inside high aspect ratio patterns encountered during LIGA processing.

LECD is generally performed with micrometer-sized insoluble anode and conductive cathode immersed in the solution containing metal ions which, once reduced, bring about the microstructures.[3-11] The feasibility of forming the microstructure is related to the following factors: the applied voltage and distance between the two electrodes,[3,5-9] the fabrication procedure, geometry,[3] rotation and vibration of the electrodes,[10,11] and the composition and additives of the electrolyte.[5] On the other hand, the shape and dimension of the microstructure are controlled by the relative motion of the anode to the cathode.[3,6,9] When the dc current is employed, the applied potential and the distance between the anode and cathode have been shown to markedly affect the growth of the microstructures. A critical voltage is required for a given anode-cathode distance, below which electrocrystallization would not occur. As the gap between the anode and cathode is decreased to a certain distance, the porous deposits prevail because the current density exceeds the limited current density.[8] This result further helps in reaching the conclusion that a constant distance between the anode tip and growing microstructure is demanded to keep the current density within the limited value throughout plating. This constant gap between the anode and the microstructure has been realized by an adaptive tip-withdrawal control.[6] The most common practice for LECD process is the feedback control that monitors the deposition current and triggers electrode positioning actuators when a current threshold is reached. However, an abrupt increase in the deposition current always occurs as a result of the closely approaching between the anode and the growing cathode. Therefore, the process in turn results in porous deposit because the current density exceeds the limit current density. And even worse, due to the repetitive deposition-withdrawal process, the microstructure exhibits a nodular structure on which the diameter varies alternatively as electroplating proceeds.[5,7] This study details the development of the nodular microstructure and its relation to voids on the surface and inside copper columns fabricated by LECD. Furthermore, a repetitive deposition-detection-withdrawal control algorithm for the movement of the anode tip is thus developed, which effectively improves the surface confinement and properties of the deposited copper microcolumns.

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Experimental

LECD.— Copper microcolumns were deposited in the solution composed of 0.5 M copper sulfate and 0.38 M sulfuric acid at 25°C via LECD method. A 25 μm Pt wire insulated in the boron-silicate tube filled with M-Bond epoxy was used as the anode. Details of the anode preparation procedure can be found elsewhere.[8] A copper disk was used as the cathode, which geometry was designed for measuring the resonance frequency of the microcolumns. Prior to electrodeposition, the copper disk was polished with emery paper up to grade 2400 and then with 1 μm alumina slurry on polishing cloth, and finally thoroughly rinsed in distilled water. To fabricate the microcolumns, the anode was connected to a micro-stepping motor stage driven by the pulse current, and the distance between the anode and cathode was set at 10 μm before the dc potential was applied.

Electrodeposition was performed potentiostatically at 3.8 V, while the movement of the anode was controlled by two types of algorithms: deposition-withdrawal and deposition-detection-withdrawal. For the deposition-withdrawal control, the anode was kept at the fixed position until a surge of current was detected, i.e., the growing microstructure contacted with the anode. The potential was then switched off and re-applied after the anode was withdrawn a distance of 10 μm away from the cathode. In the case of deposition-detection-withdrawal control, the potential was reduced to 0.1 V when the microstructure grew to a distance around half of the original separation between the two electrodes. The anode was then driven backward until it touched the microstructure to detect the position of the tip of the microcolumn and withdrew again to a distance of 10 μm away from the microstructure. The length of the microstructure grown during each deposition-detection-withdrawal cycle can be measured by subtracting the detection movement from the withdrawal movement, i.e., 10 μm in this present design. Consequently, the length of the microcolumn, which was set to be ~2000 μm, was controlled by either the total movement of the anode for the deposition-withdrawal control or the accumulated length grown during each cycle for the deposition-detection-withdrawal mode.

Microstructural characterization.— The overall morphology and detailed surface morphology of the microcolumn were investigated using a scanning electron microscope (SEM). An optical microscope was employed to examine the cross-section of the microstructure. To prepare the cross-sectional specimen, the microstructure was removed from the cathode and placed longitudinally with an adhesive tape onto a copper block, and subsequently embedded in M-Bond epoxy. After being cured at 90°C for 0.5 h, the microstructure was polished down to 0.05 μm alumina slurry, rinsed in distilled water and chemically etched in 30 vol % ammonia solution.

Resonance frequency measurement.— The copper substrate with grown microcolumn which is in cantilever configuration as viewed horizontally was mounted on the output head of a piezoelectric actuator. The actuation of the piezoelectric actuator excited the periodic movement of the copper substrate and, thereby, the lateral vibration of the cantilever beam. A laser displacement probe (Polytec MSV-300) was employed to measure both the velocities of the copper substrate and the tip of the cantilever beam, respectively. Upon sweeping the periodic actuation over a predetermined frequency span, the transmissibility spectrum of the cantilever beam due to base excitation could be obtained. It was from the peak with maximum transmissibility of the spectrum that the resonance frequency of the cantilever beam was found.

Electric field analysis.— The electric field distribution across Pt anode and copper plate cathode was calculated using ANSYS software based on the assumption that the electrolyte composition is uniform and the solution electrical resistivity remains constant during electroplating. Compared with the ϕ25 μm Pt anode, the copper cathode can be treated as a plate of infinite size. As grown by localized electric field, the geometry of the cathode evolved into a column that can be considered as a tip electrode. To account for this geometric change, the electric field distribution was also calculated as the column grew.

Results and Discussion

Microstructure of copper columns.— Figures 1a and b show the morphology of the columns made by the two different control methods. Followed by an initial transitional stage in which the diameter of the column decreased with continued electroplating, a steady-state stage was reached when the average diameter of the column grown by the deposition-withdrawal and the deposition-detection-withdrawal method was around 18 and 20 μm, respectively, and changed little as electroplating proceeded. This smaller average diameter as compared to the diameter of Pt anode is probably due to the fact that the separation between the anode and growing deposit, i.e., 10 μm during the beginning of each deposition cycle is comparable to the tip-deposit end spacing, i.e., 25 μm. Figure 1 also shows that the column deposited with the deposition-withdrawal control method displayed a nodular structure which had a pitch of the same distance as that of each withdrawal. In contrast, the deposition-detection-withdrawal method effectively eliminated the nodular structure associated with the repetitive deposition. Furthermore, both columns exhibited a smooth surface on which voids were hardly observed though vigorous gas evolution was noted during electroplating. Figures 2a and b show the longitudinal cross-sections of the columns presented in Fig. 1a and b, respectively. Several relatively large voids were observed inside the column made by the deposition-withdrawal control method (Fig. 2a). Figure 2a also shows that these voids apparently resided on the nodular boundaries. The voids at the boundaries indicated the deposit was quite porous as the column surface approached the anode tip. This is consistent with the in situ observation on the growth of copper columns using coherent microradiology with synchrotron irradiation.[8] That is, when the distance between the anode and the growing deposit approaches a critical value, the current increases abruptly and a porous deposit forms. Although the surface of the column was sound and free of voids when observed by SEM, the porous structure formed upon the current surge was apparently not completely filled during the subsequent electroplating and remained as internal voids at nodular boundaries. To avoid the formation of the porous deposit due to either the direct contact or too close separation of the growing deposit and anode, the deposition-detection-withdrawal control method was adapted and was able to fabricate the copper column free of internal and surface voids (Fig. 2b). An adaptive tip withdrawal technique has been shown to enhance the geometry confinement and reduce the porosity of copper microcolumns prepared by LECD.[6] In this process, the tip withdrawal is controlled to be relatively equal to the deposition rate by monitoring the tip current gradient while a constant dc voltage is applied during deposition. This control significantly reduces the risk of short-circuit contact, and thereby the porosity of the deposit. The deposition-detection-withdrawal control method used in the present study can totally avoid the short-circuit contact and also enhance the replenishment of

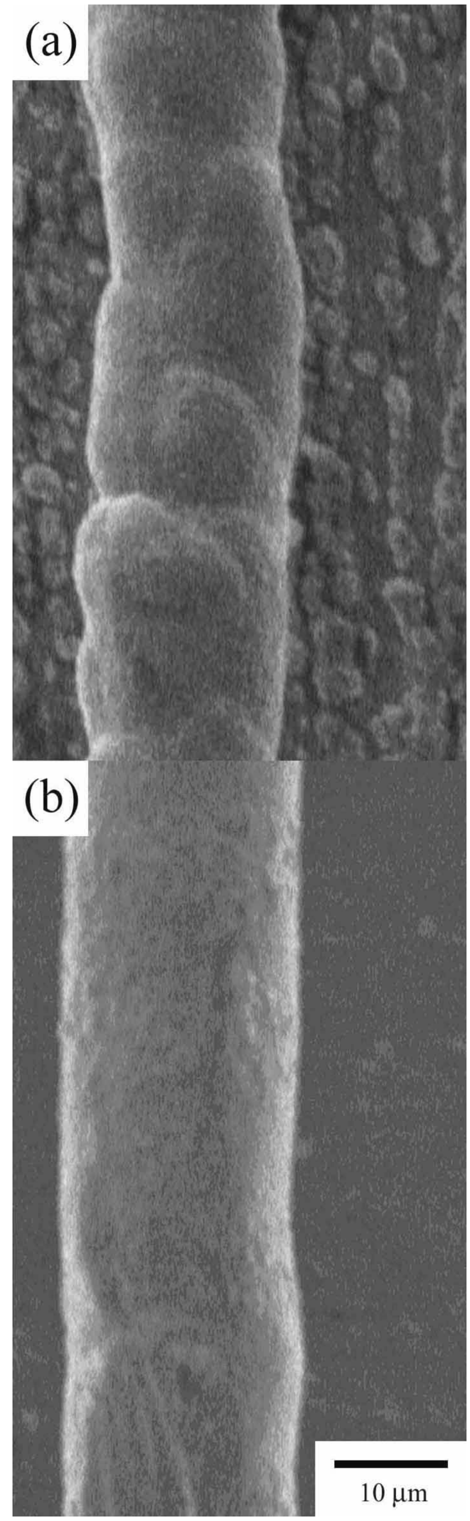

Figure 1. Morphology of the columns made by the two different control methods, (a) deposition-withdrawal control method and (b) deposition-detection-withdrawal control method.

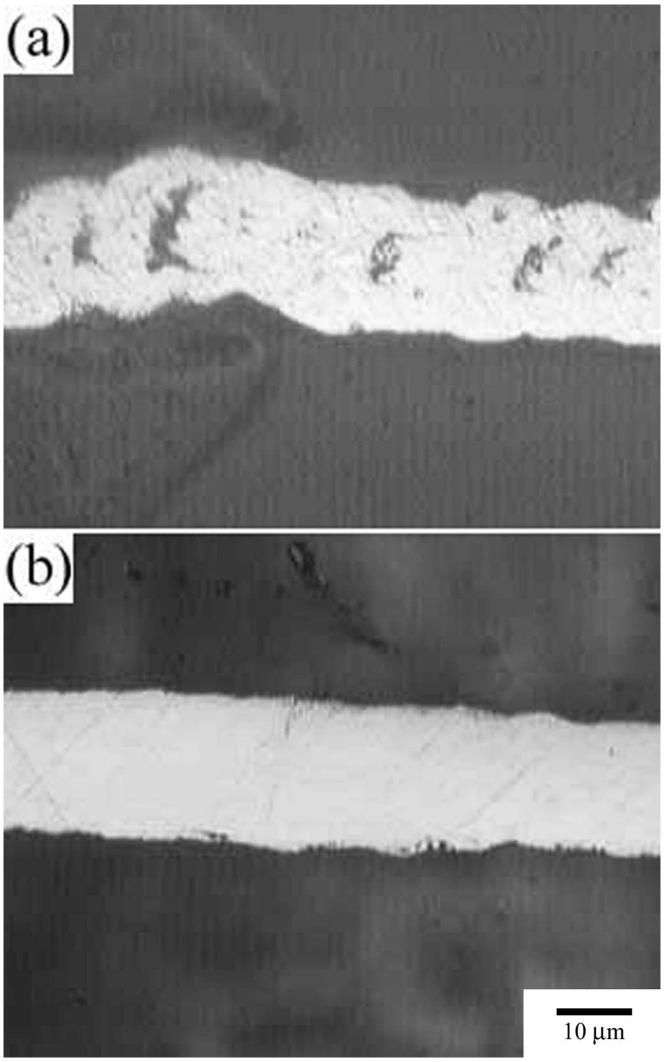

Figure 2. Longitudinal cross sections of the columns fabricated by (a) deposition-withdrawal control method and (b) deposition-detection-withdrawal control method.

copper ions to the gap between the two electrodes. Both contribute to the improved surface quality and the reduced internal voids of the deposit.

Electric field distribution.—Figure 3a shows the electric field distribution across the anode tip and the plate cathode during the very beginning of the electroplating. The electric field was apparently concentrated around the mutual axis of the two electrodes and exhibited an axisymmetry. This is in good consistence with the results shown in Ref. 3 and 7, which calculate the electric field distribution using a finite element method (MSC EMAS) and a boundary element method, respectively. Figure 3b shows a transverse electric field distribution profile on the surface of the cathode. The electric field had a maximum at the center and decreased rapidly at a distance away from the center. The distribution profile for a cutoff value of 10^5 V/m had a diameter of ~40 μm which was close to the diameter of the deposit. As copper grew with continued electroplating, the effective shape of the cathode changed from plate to column. The evolution of the deposit into a column during LECD has been detailed via the theoretical simulation based on a boundary element method in conjunction with the experimental verification for the copper columns grown at 5, 15, and 20 μm in deposition height, respectively.[7] Figure 4 shows that the electric field became more concentrated toward the mutual axis when the deposit re-

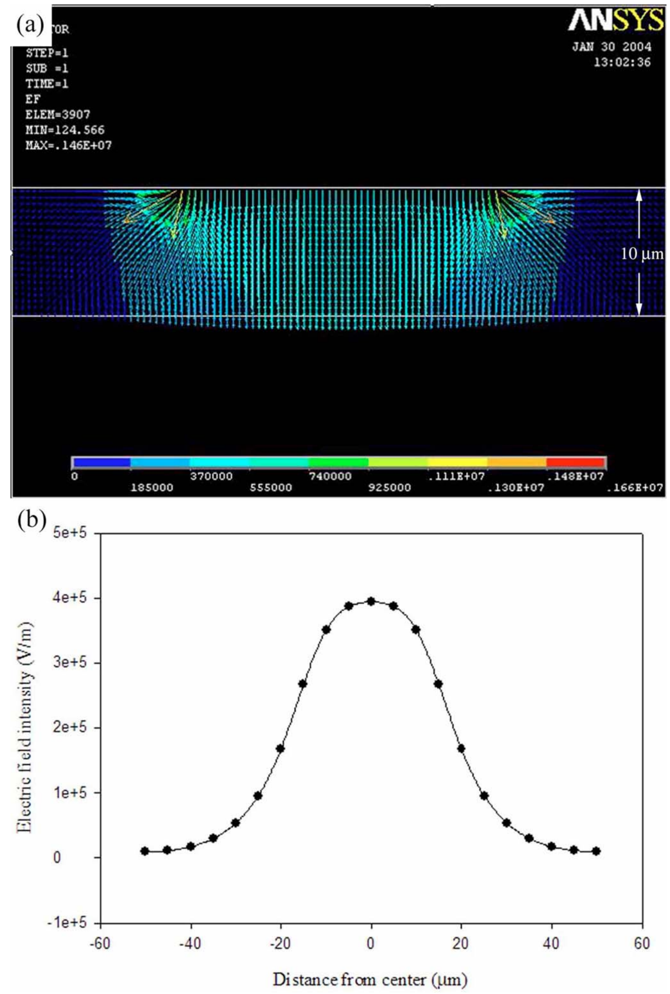

Figure 3. Electric field distribution across the anode tip and the plate cathode during the very beginning of electroplating. (a) Electric field distribution of the whole domain. (b) Electric field profile on the surface of the cathode.

sembled a column of 20 μm in diameter. Interestingly, the diameter with the same cutoff electric field of 10^5 V/m was reduced to 20 μm, which was equal to the diameter of the grown deposit and changed little as electroplating continued. It is not immediately clear why an electric field of 10^5 V/m is necessary for the electrocrystallization and growth of copper. This critical electric field, however, can provide an additional basis for estimating the lateral dimension of the microstructure. During each deposition cycle, the maximum electric field was approximately 8×10^5 and 4×10^6 V/m when the deposit grew to a distance of 1 and 5 μm from the anode tip, respectively. This highly intense electric field can explain the formation of porous deposit when the growing deposit approaches the anode tip.[6,7]

Properties of copper cantilever beam.—The first-mode's resonance frequency of the copper column was ~2800 Hz from measurements of several specimens. The corresponding apparent Young's modulus was 176 GPa as calculated by

$$\omega_n = (\beta_n l)^2 \sqrt{\frac{EI}{\rho l^4}} \qquad [1]$$

where ω_n is the circular frequency of the first-mode resonance, $(\beta_n l)^2 = 3.52$ is the parameter of the first-mode resonance for cantilever beam, l and I are, respectively, the length and moment of inertia of the beam, ρ the linear density of the deposit, which is equal to the mass density times the cross-section of the beam. The

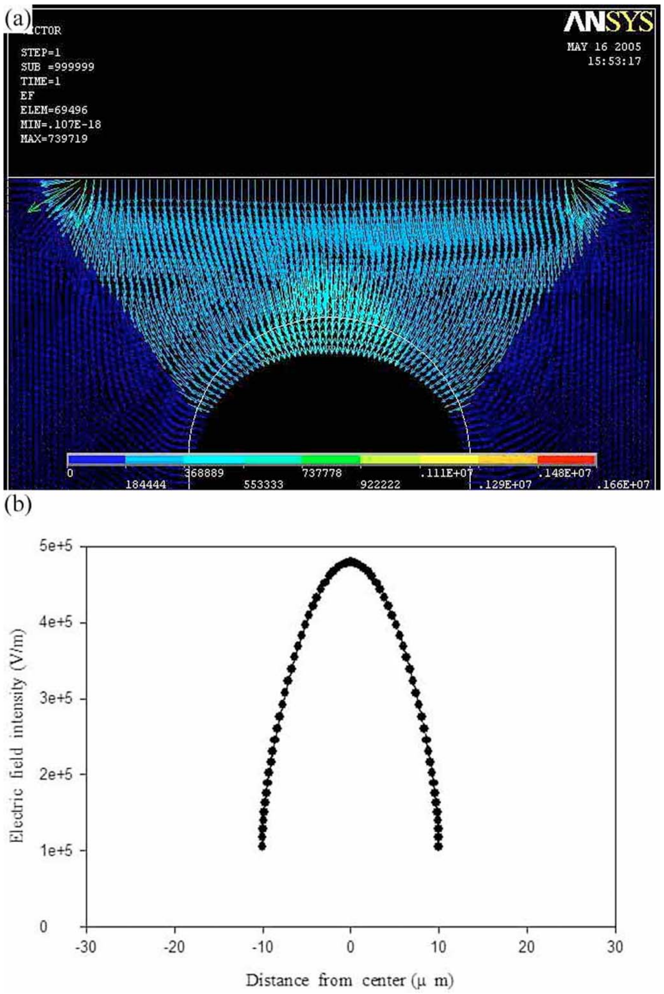

Figure 4. Electric field distribution across the anode tip and the well grown cathode. (a) Electric field distribution of the whole domain. (b) Electric field profile on the surface of the cathode.

measured apparent Young's modulus of copper column as mentioned previously is roughly 47% higher than that of the bulk copper, i.e., 120 GPa. Because Young's modulus is a materials constant related mostly to atomic bonding strength rather than the composition, factors must account for the discrepancy in Young's modulus.

First, voids inside the column reduce its effective density, thus lowering the apparent Young's modulus. This can be seen from Eq. 1 that under the same measured resonance frequency ω_n the apparent Young's modulus is directly in proportion to the effective density. Second, the geometry of the column can contribute to the lower modulus associated with the column. Based on the electric field distributions during the transitional and steady-state stages (Fig. 3 and 4), the copper column can be described as the schematic representation (Fig. 5) consisting of a conical part directly adherent to the substrate and a nodular part which diameter changes periodically. The former attributes to the relatively divergent electric field distribution during the early stage of electroplating and the latter forms after the diameter of the column approaches that of the anode tip. The diameter of the column along longitudinal axis can thus be expressed as

$$d = \begin{cases} d_0 - mx, & x < L_0 \\ \bar{d} + d_1 \cos\dfrac{2\pi x}{p}, & x \geq L_0 \end{cases} \qquad [2]$$

where L_0, d_0, and m are, respectively, the length, maximum diameter and slope of the conical part; $\bar{d}$ the average diameter, d_1 the amplitude, and p the pitch of the nodular portion. By taking $L_0 = 90\ \mu m$, $\bar{d} = 18\ \mu m$, $d_1 = 2\ \mu m$, $p = 10\ \mu m$ for most of the copper columns fabricated by the deposition-withdrawal control method and using an inhouse finite element code, the first-mode's resonance frequency as a function of d_0 is obtained as shown in Fig. 6. This result shows that the resonance frequency has an ~7% increase as d_0 is changed from 18 to 50 μm. This increase corresponds to a 14.2% increase in the apparent Young's modulus.

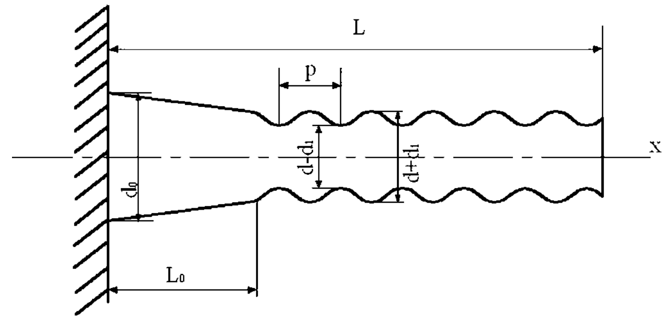

Figure 5. Schematic representation of the deposited microcolumn fabricated by the deposition-withdrawal control method.

Thus, both the decreases in the deposit density and the geometry deviation of the column from prismatic beam contribute to the higher apparent Young's modulus measured. And most importantly, the two contributions are closely related to the electric field distribution. It is crucial, therefore, to accurately control the proper electric field across the two electrodes during electroplating, particularly maintain a constant and not too close distance between the two electrodes during the growth of copper columns. The successful control in the gap distance between the electrodes can avoid the current surge from the contact of the two electrodes. This has been realized by the measurement of the Young's modulus of the copper column fabricated by the deposition-detection-withdrawal control method.

Based on the Young's modulus of the bulk copper and the conical base configuration of the microcolumn, Table I presents the comparison between the calculated mass densities of the microcolumns for the two deposition methods. It clearly shows the proposed deposition-detection-withdrawal control method improved the percentage of the effective density of the microcolumn. The calculated effective mass density increased from 27.7% lower than the bulk

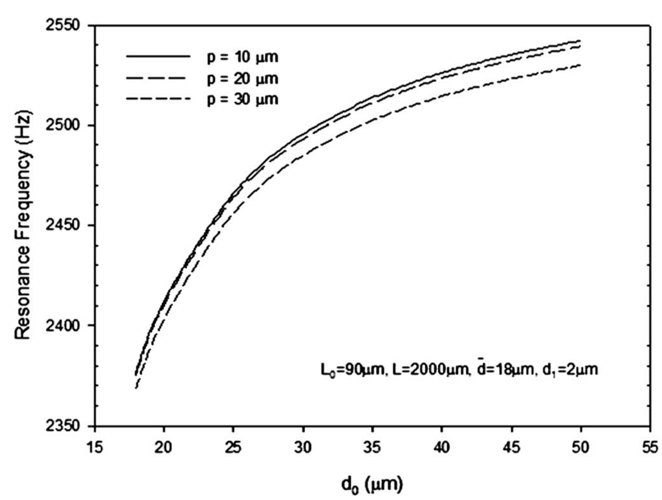

Figure 6. Simulated first-mode's resonance frequency of the microcolumn as a function of d_0 and p.

Table I. Comparison between the calculated mass densities of the microcolumns for the two deposition methods.

Deposition method	Measured first mode's resonance frequency (Hz)	Calculated mass density (kg/m^3)	Theoretical bulk mass density (kg/m^3)	Percentage difference (%)
Deposition-withdrawal control method	2800	6458	8930	−27.7
Deposition-detection-withdrawal control method	2300	8537	8930	−4.4

material for its deposition-withdrawal control method counterpart to 4.4%. This improvement is consistent with the reduction in void content seen in the micrographs of Fig. 2.

Conclusions

This study correlates the structure and properties of copper microcolumn to the movement of the anode relative to the growing cathode during localized electroplating. The short-circuit contact results in microvoids residing on the nodular boundaries that develop due to the repetitive backward withdrawal of the anode as electroplating proceeds. Both the geometry and void content of the microcolumn affect the first-mode's resonance frequency and the resulting apparent Young's modulus of the copper microcolumn. The result signifies that optimal control in the relative movement of the electrodes, particularly free from the risk of short-circuit contact, can greatly improve the properties of the microstructure. This has been successfully fulfilled in the present study by a deposition-detection-withdrawal control method. In this proposed method, for avoiding the short-circuit contact, the movement of the anode is triggered forwards and then backwards at 0.1 V when the microcolumn grows to a length of approximately half of the initial separation between the anode and cathode. It is shown that the improved microcolumn demonstrates a decrease in apparent void content from 27.7 to 4.4%.

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