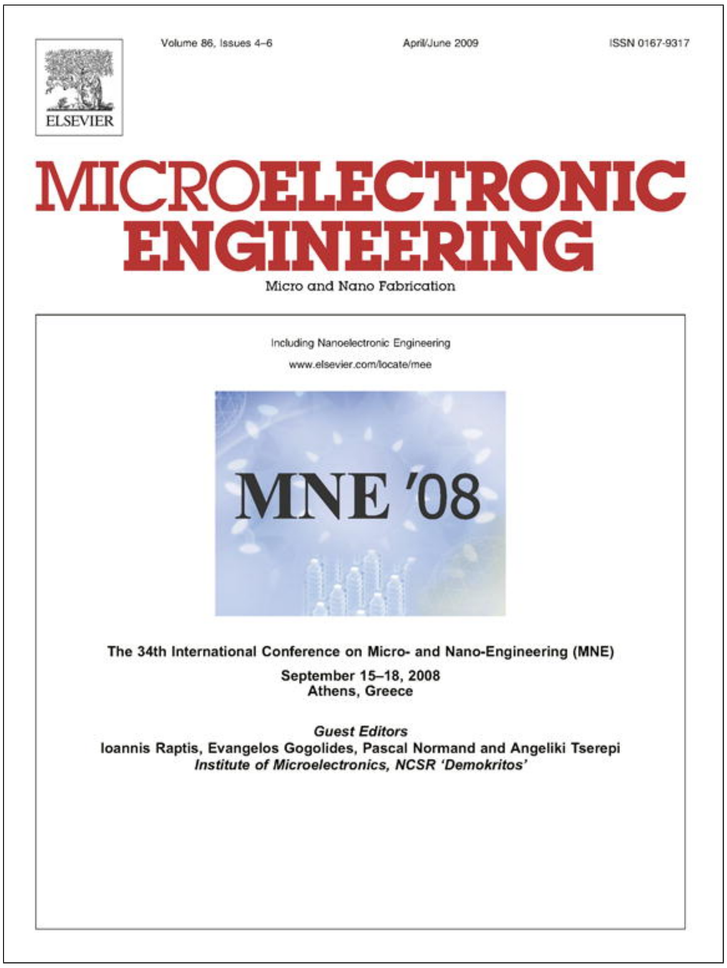
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Topography-sensitive copper deposition in supercritical solutions

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ABSTRACT

Topography-sensitive deposition, a preferential growth mode in a narrow concave feature, of copper in supercritical solutions is reported. Experiments were carried out in supercritical carbon dioxide at 13 MPa with a maximum temperature of 230 °C, using bis(diisobutylmethanate)copper ($Cu(dibm)_2$) as a precursor. Cu was preferentially deposited in narrow cylindrical features with a diameter less than 100 nm. Copper deposits were mostly rod-like and single-crystalline. In larger features deposition occurred within the inside corner of the features. Nonmetallic residues were also found at locations having a small curvature. Through different visualization experiments, the residues were identified as an unreacted precursor. From these observations, it was concluded that the topography-sensitive deposition proceeds through a capillary condensation of the precursor that is dissolved in the supercritical carbon dioxide at a high concentration, following the conversion to metallic copper.

1. Introduction

A supercritical fluid is a dense medium that a substance has above its thermodynamic critical point, and it behaves both like a liquid and a gas. Supercritical CO_2 (the critical point of CO_2 is 7.4 MPa and 31.1 °C) has several unique features, such as zero-surface tension, solvent capability, good diffusivity, and low viscosity.

It has been demonstrated that thin film deposition in supercritical CO_2 is capable of filling or coating metals and oxides in very narrow features [1–6]. In this technology, organometallic compounds are thermally-reacted in supercritical CO_2, usually with a reaction reagent such as hydrogen and oxygen. Formation of electrodes and interconnects of ultra large-scale integrated circuits (ULSIs) [1,2,5,6] and embedding metal in carbon nanotubes [3] has been reported, taking advantage of the good filling capability of this method. Such a positive filling performance has generally been attributed to the excellent penetration capability of the supercritical CO_2 [2,4].

Previous studies have reported that thin film deposition in supercritical CO_2 occur usually in a very conformal manner [2]. However, for very narrow features below approximately 50 nm, it has been reported that deposition proceeds without forming seams or voids [3–7]. This somehow defy our belief in thin film deposition chemistry, because the conformal deposition usually ends up with the formation of seam or void in narrow features due to mass flux crowding at the edge of a feature portal. It seems that narrower features can be filled preferentially using this technique, which is an ideal property as bottom-up nano fabrication.

In this paper, we demonstrate preferential growth of Cu nano rods in a narrower concave topography. The origin of this phenomenon is discussed along with the characterization of Cu nanorods.

2. Experimental

Deposition experiments were carried out using a batch arrangement having a dead-end reactor [8]. The precursor used was bis(diisobutylmethanate) (bis(2,6-dimethyl-3,5-heptanedionato)copper(II), $Cu(dibm)_2$, CAS 17653-77-9). $Cu(dibm)_2$ is a dark-greenish solid at normal temperature and pressure. The precursor, weighed to a concentration of 0.03 mMol/cm^3 (25 mg/cm^3 of cell volume), was placed at the bottom of a pressure-resistant 316 stainless steel cell (2.2 cm^3 vol.) and a substrate was placed near the precursor in facedown manner. No stirring device was employed. The cell was then filled with gaseous hydrogen to 1 MPa and was heated with a heating mantle. Pressurized liquid CO_2 was then added to the cell with a high pressure pump specially designed for supercritical CO_2 chromatography (JASCO PU2080 mod), and the cell was heated to 230 °C and 13 MPa at a ramp rate of approximately 10 °C/min and held for 10 min, following quick depressurization and cooling. Si wafer pieces (approximately 9 × 9 mm), having a test structure for ULSI interconnect evaluation and being coated with atomic-layer deposited TiN, were used as substrates. The deposited copper were observed with a JEOL JSM 6500F field-emission gun scanning electron microscope (SEM) and a Hitachi HD 2300C scanning transmission electron

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microscope (STEM), both equipped with an energy-dispersive X-ray spectrometer (EDX).

3. Results and discussion

Fig. 1 shows a cross-sectional SEM image of nanorods. It can be observed that the rods grew perpendicularly and selectively in holes of approximately 100 nm in diameter. The growth was found to occur in a bottom-up manner. Such selective growth was observed only in small features. EDX analyses showed these rods were copper. Top views show that small holes were fully filled with Cu. Larger features were not fully filled, whereas the nucleation had started at the corners (Fig. 2). Cu was not grown in the large hole on the top-right (arrowed). A small non-copper residue, nonmetallic in appearance, was found at a corner of this hole. An EDX spectrum showed that this residue contains copper, carbon, and oxygen. We presume that this residue is an unreacted Cu precursor. Fig. 3 shows secondary electron (SE) and z-contrast (ZC) images of a Cu rod observed with the STEM. The SE image shows that the hole is filled to the bottom (arrowed), whereas the same area exhibited a dark contrast in the ZC image, indicating that this area contains more light elements. The EDX spectrum taken from this area showed intensive carbon and oxygen peaks, similar to the one shown in Fig. 2.

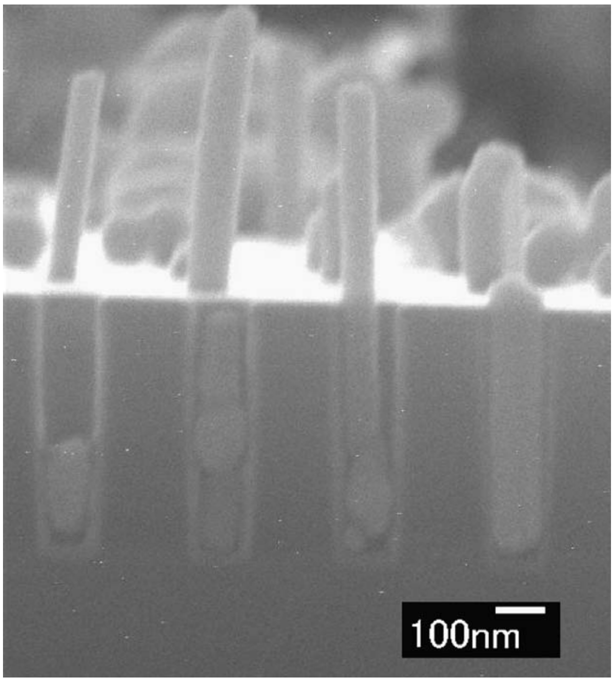

Fig. 1. Cu nanorods grown in narrow holes.

We presume that the origin of this selective growth is the “topography-sensitive” mechanism. A supercritical fluid is a very dense medium. The precursor dissolved has a very high partial, even higher than its vapor pressure. The precursor has a much lower vapor pressure than CO_2, and therefore, in supercritical CO_2, it can condense in small features through the capillary condensation mechanism. The capillary condensation occurs better in features having a smaller curvature; as a result the precursor condenses at the bottom of the small features and at the bottom corner of the large features.

In the preceding study we confirmed that $Cu(dibm)_2$ condenses in nanopores in supercritical CO_2 at an elevated temperature of 150 °C [8]. In order to study that the condensation of $Cu(dibm)_2$ can occur in holes used in the present study, we performed the following experiments. In the first confirmatory experiments, $Cu(dibm)_2$ (250 mg) was placed in a fixed-volume view cell (approximately 10 cm^3) filled with supercritical CO_2 of 8 MPa, and the temperature was rose from 40 to 170 °C with sheath heaters that were equiangularly embedded in the cylindrical cell wall. No stirring was carried out. This arrangement is same as our deposition experiments in terms of supply way of the precursor. The precursor amount per cell volume is the same as in deposition experiments, allowing a good comparison. The $Cu(dibm)_2$ and the fluid were monitored with a charge-coupled device (CCD) camera through a window of the view cell during the temperature rise. It was observed that the $Cu(dibm)_2$ melted at approximately 90 °C

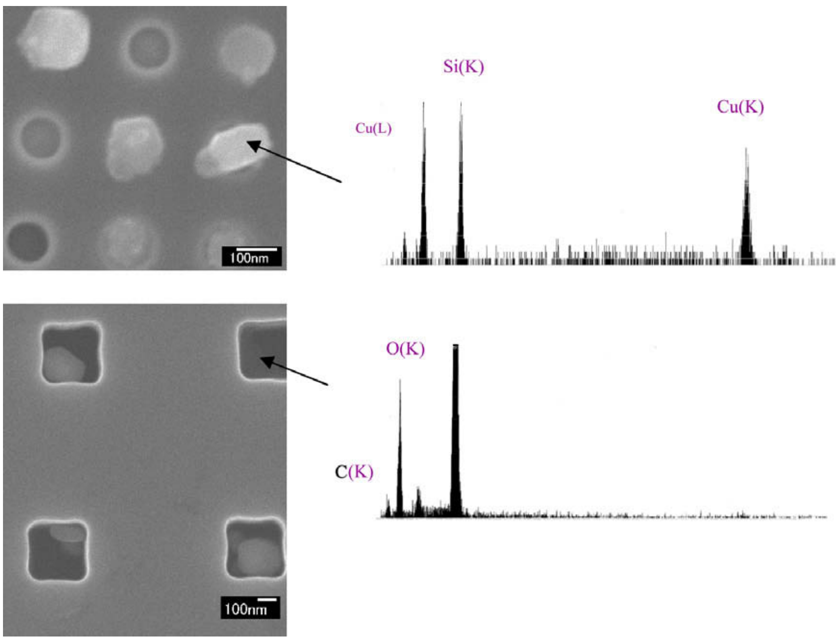

Fig. 2. Top views of Cu deposits formed in smaller (left) and larger (right) holes. The spectra are EDX spectra taken from the arrowed particles.

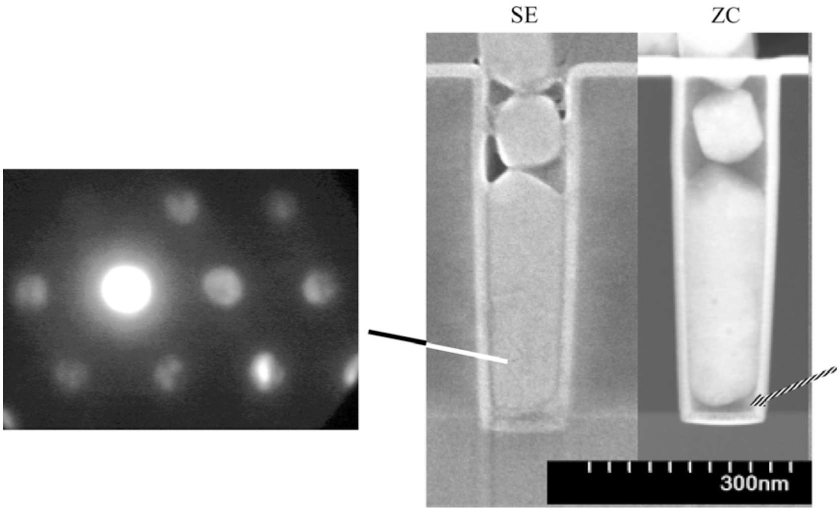

Fig. 3. Cross-sectional secondary electron (SE) and z-contrast (ZC) images of Cu deposits formed in a hole. The nano-beam diffraction pattern was taken from the pointed grain. For the arrowed part, please refer to the main text.

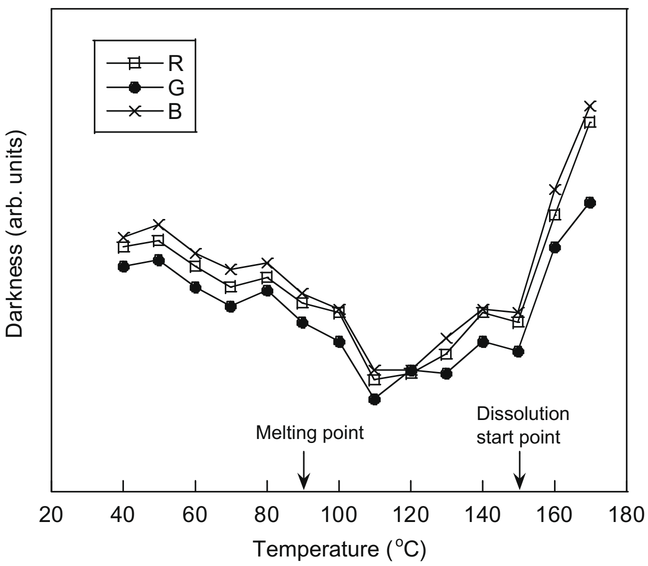

Fig. 4. RGB color contrasts of the fluid as a function of the temperature.

and began to dissolve in the fluid at approximately 150 °C. Fig. 4 shows the red (R), green (G), and blue (B) signals from the CCD camera, averaged over an area of about 100 mm^2 of the window center, plotted against the cell temperature. The RGB darkness started to increase at a temperature of approximately 150 °C, due to the coloration of the supercritical CO_2 fluid. The green signal increased at a significantly less degree, indicating that the fluid became greenish, reflecting the color of $Cu(dibm)_2$. Another important observation was that the melted (liquid) precursor remained in the cell even after the dissolution started. This suggests that $Cu(dibm)_2$ can easily condense in narrow features under its near-saturation conditions.

The next confirmatory experiments were carried out in the same manner as the Cu deposition experiments but without hydrogen and with temperatures of 140 and 155 °C. Note that these temperatures are far below the deposition starting temperature of 180 °C (The incorporation of hydrogen decreases the Cu deposition temperature, therefore Cu is expected not to be formed at these temperatures). Nonmetallic residues were seen at the corners of the hole and in a nano trenche when the temperature was raised to 155 °C (Fig. 5b), whereas no residues were observed for the maximum temperature of 140 °C (Fig. 5a). Therefore, it is now clear that $Cu(dibm)_2$ can condense in a feature having a small curvature

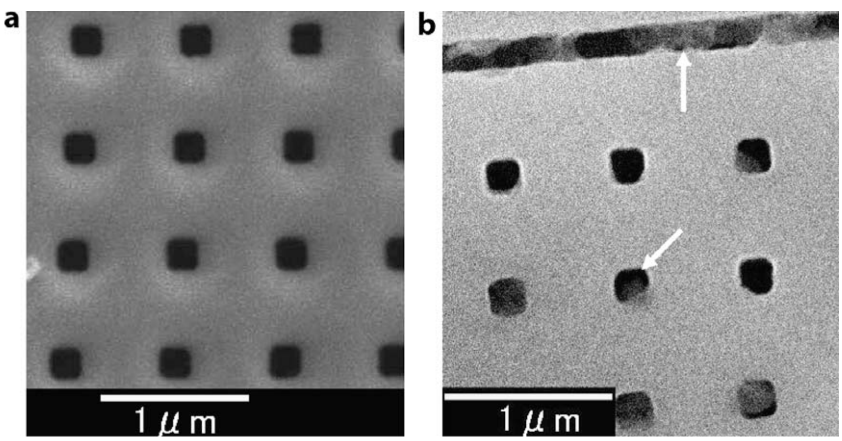

Fig. 5. Top views of holes exposed to a supercritical fluid with $Cu(dibm)_2$ at 140 °C (a) and 155 °C (b).

when the temperature is increased above its dissolution temperature of 150 °C.

In the actual deposition experiments, the temperature was raised to 230 °C. At such a high elevated temperature, the density of the fluid decreases and the precursor solubility decreases. As a result condensation may occur easily. The Cu deposition reaction that occurs concurrently or after the condensation complicates matters. Either the direct conversion of the condensed precursor or the Cu nucleation of the fluid that is in contact with the condensed precursor is likely.

It is presumed that the rod formation observed in the present experiments is a very dynamic process, as suggested from the unidirectional shape of Cu. Generally speaking, common metals like copper grow isotropically and have a round shape. The diffraction pattern of the Cu grain shows that the grain is a single-crystalline (Fig. 3 left). Single crystals can be grown in an anisotropic and kinetic manner; this behavior can explain why the Cu rods overgrew unidirectionally, as seen in Fig. 1. The dissolution and condensation of the precursor also proceeds dynamically and locally, apart from chemical equilibrium. The dynamics of the process makes analytical interpretation complicated, and further study on this subject is left for our future work.

4. Conclusion

This paper reported a preferential growth of Cu in a narrow concave feature, namely topography-sensitive growth, via hydrogen reduction of an organometallic Cu precursor that was dissolved in a supercritical CO_2 fluid. It was found that the growth occurred in narrow capillaries and corners that have a small curvature. Residues containing carbon, oxygen, and copper, presumably unreacted precursors, were found at some of these locations. From supporting experiments using a window view cell, the formation of the residue at these locations was believed to occur in a supercritical solution that is nearly saturated with a precursor having a low solubility to the solution. The Cu grains were presumably single-crystalline, and grew in an anisotropic manner leading to a rod-like shape. This behavior suggests that the topography-sensitive growth is a dynamic process. In principle, the topography-sensitive growth mode proceeds better in the narrower features, which can be a key to solve the limit of continued downscaling in micro and nano device processing.

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