Seedless Growth of Free-Standing Copper Nanowires by Chemical Vapor Deposition

Hyungsoo Choi* and Sung-Ho Park[†]

Micro and Nanotechnology Laboratory and Department of Electrical and Computer Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

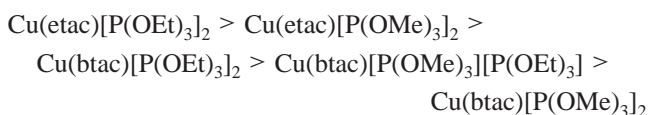Received February 12, 2004; E-mail: hyungsoo@uiuc.edu

Metal nanowires have attracted much attention due to their potential use as interconnects in future nanoelectronics and application possibilities for magnetic devices, nanosensors, electron emitters, and many more. Among the various physical and chemical methods developed for the fabrication of metal nanowires, the chemical/electrochemical methods utilizing templates, such as membranes, nanostructures, and surface step-edges, are the more widely used approaches to preparing free-standing metallic nanowires.[1−20]

Most of these methods, however, require removal of the templates to produce free-standing metal nanowires. A method using step-edges as the templates was reported to grow nanowires removable from the template surfaces. Nanowires of copper, nickel, silver, gold, and palladium have been prepared by such a method by electrodepositing Mo oxide wires at the step-edges on a graphite surface followed by reduction in H_2; however, they were composed of rough grains.[6,20] The metal nanowires of Au, Ag, Pd, and Pt grown by a redox chemistry method using $LiMo_3Se_3$ wires as sacrificial templates also produced nanowires composed of grains.[16] Herein, we report seedless growth of free-standing copper nanowires by chemical vapor deposition (CVD) at low temperatures. The process requires neither catalysts nor templates to yield crystalline copper nanowires which are vertically aligned on the substrate surfaces.

Previously, we have reported Cu(I) *tert*-butyl 3-oxobutanoate complexes, (btac)CuL, where L = Lewis base, as precursors to deposit copper metal by CVD.[21] Among them, (btac)CuP(OMe)$_3$ was especially attractive as a CVD precursor since it was isolated as a stable, volatile liquid and deposited highly pure copper thin films with smooth and dense surface morphology. In this study, we prepared Cu(I) *tert*-butyl 3-oxobutanoate complexes containing two phosphite ligands and deposited copper films using them as precursors. The thermal stability of these Cu(I) complexes was greatly enhanced as additional phosphite was coordinated to the metal and as the btac ligand was replaced with an etac, where etac = ethyl 3-oxobutanoate. Interestingly, the grain structures of the deposited films were affected significantly by the thermal stability of the Cu(I) complexes. In contrast to (btac)CuP(OMe)$_3$, Cu(btac)-[P(OMe)$_3$]$_2$ produced films of larger grains which were elongated and exhibited columnar growth as the precursor stability increased. Eventually, copper nanowires were produced when (etac)Cu-[P(OEt)$_3$]$_2$ was used as the precursor.

The Cu(I) alkyl 3-oxobutanoate complexes, (btac)CuL$_2$ and (etac)CuL$_2$, where L = P(OMe)$_3$ and P(OEt)$_3$, were prepared by mixing 1 equiv CuCl with 2 equiv phosphite in THF followed by the addition of 1 equiv Na(etac) in THF.[21,22] The Cu(I) complexes were isolated as volatile liquids.[23] The thermal stability of the Cu-

(I) complex increased in the following order:

$$Cu(etac)[P(OEt)_3]_2 > Cu(etac)[P(OMe)_3]_2 >$$
$$Cu(btac)[P(OEt)_3]_2 > Cu(btac)[P(OMe)_3][P(OEt)_3] >$$
$$Cu(btac)[P(OMe)_3]_2$$

CVD experiments were carried out using the Cu(I) complexes as the precursor in a glass cold-wall reactor to investigate the grain growth of the deposited copper films. Typically, the precursor was evaporated onto a Si(111) substrate at a temperature range of 200−300 °C under 0.1−1.0 Torr using argon as a carrier gas. No reducing agent such as hydrogen was used.

Panels a−c of Figure 1 show the cross-sectional SEM images of the copper films grown at a substrate temperature of 250 °C for 30 min using Cu(btac)[P(OMe)$_3$]$_2$, Cu(btac)[P(OEt)$_3$]$_2$, and Cu-(etac)[P(OMe)$_3$]$_2$ as precursors. The grains in the films deposited from Cu(btac)[P(OEt)$_3$]$_2$ show more tendency to grow vertically compared to those from Cu(btac)[P(OMe)$_3$]$_2$ without noticeable growth in the lateral direction. As the precursor switches to Cu-(etac)[P(OMe)$_3$]$_2$, the grain growth continues to give a distinctive columnar structure as shown in Figure 1c. With this precursor, the grains grow not only vertically but also laterally. Panels d and e in Figure 1 show the top views of the films deposited from Cu(btac)-[P(OEt)$_3$]$_2$ and Cu(etac)[P(OMe)$_3$]$_2$, respectively, which indicate the lateral growth of the grains in the film deposited from the latter precursor. It is interesting to observe the columnar grain growth as the precursor switched from Cu(btac)[P(OMe)$_3$]$_2$ to Cu(btac)-[P(OEt)$_3$]$_2$ and both columnar and lateral growth as the precursor
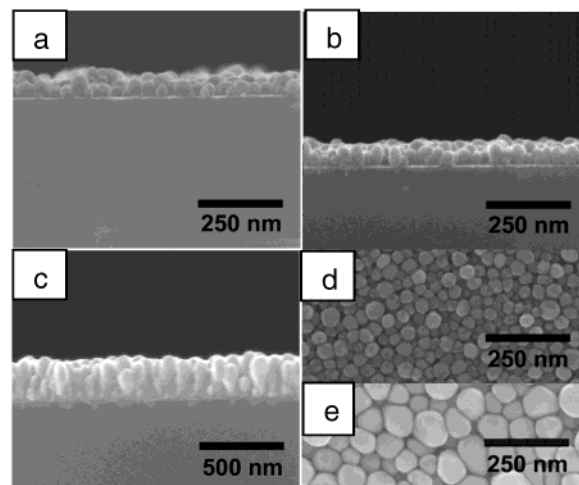

Figure 1. (a−c) Cross-sectional SEM images of copper films deposited from Cu(btac)[P(OMe)$_3$]$_2$, Cu(btac)[P(OEt)$_3$]$_2$, and Cu(etac)[P(OMe)$_3$]$_2$ at 250 °C. (d,e) Top views of the films shown in (b) and (c), respectively.
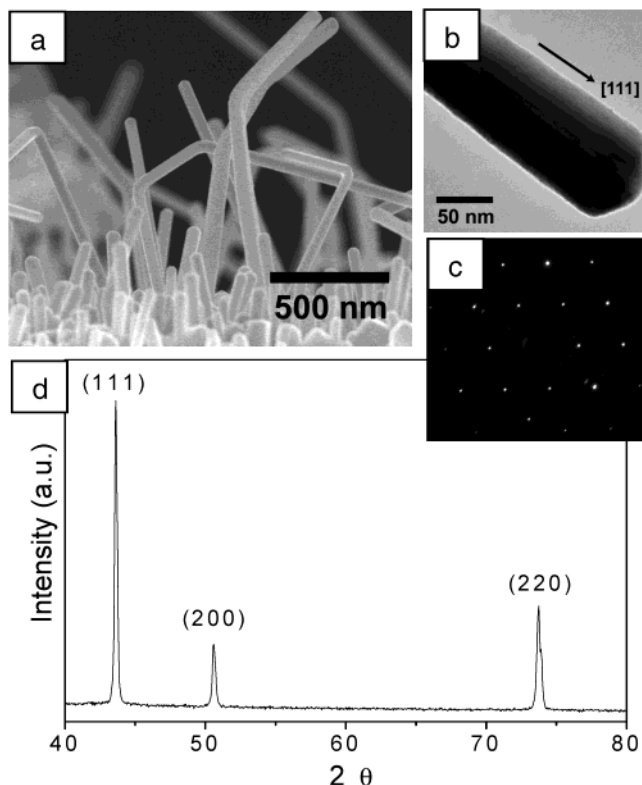

Figure 2. (a) SEM image, (b) TEM image, (c) [110] zone diffraction pattern, and (d) XRD pattern of the copper nanowires grown at 250 °C.

was switched from Cu(btac)[P(OEt)$_3$]$_2$ to Cu(etac)[P(OMe)$_3$]$_2$. The retarded nuclei formation caused by the enhanced precursor stability lends support to the grain growth observed here. The copper films deposited from these precursors were analyzed by XPS and XRD and found to be highly pure and crystalline.

When Cu(etac)[P(OEt)$_3$]$_2$ was used as a precursor, which exhibited the highest stability among the Cu(I) precursors studied, copper nanowires were produced. Figure 2a shows an SEM image of the free-standing copper nanowires grown from Cu(etac)-[P(OEt)$_3$]$_2$ on a Si(111) substrate at 250 °C for 30 min. The TEM image and diffraction patterns shown in Panels b−d of Figure 2 indicate that the copper nanowires are highly crystalline and grow in the [111] orientation with a highly oriented (111) surface. The copper nanowires can be grown on substrate surfaces other than Si.

The diameters of the copper nanowires are in the range of 70−100 nm, which are about the same as those of the grains in the film deposited from Cu(etac)[P(OMe)$_3$]$_2$. The lengths of the copper nanowires can be controlled by the processing parameters such as deposition time and precursor feed rate. With the only difference between Cu(etac)[P(OEt)$_3$]$_2$ and Cu(etac)[P(OMe)$_3$]$_2$ being the phosphite ligands, that the former gave nanowires and the latter gave films was intriguing. We have observed that the grains grew preferentially in the columnar direction as the precursor was switched from Cu(btac)[P(OMe)$_3$]$_2$ to Cu(btac)[P(OEt)$_3$]$_2$. Likewise, the preferential grain growth in the columnar direction occurred so dominantly, and nanowires evolved as the precursor was switched from Cu(etac)[P(OMe)$_3$]$_2$ to Cu(etac)[P(OEt)$_3$]$_2$. Although it may be fortuitous that the phosphite ligands relate to the columnar growth and the anionic ligands to both the columnar and lateral growth,

the precursor stability is a crucial factor for the directional growth of the grains. Further investigation is necessary to elucidate the mechanism of the grain growth that specifically gives rise to the driving force responsible for the evolution of nanowires from columnar structure. In particular, the role of ligands needs to be investigated in the CVD process of the present Cu(I) precursors including adsorption, decomposition, and nuclei formation.

In summary, copper nanowires were grown by a CVD process using Cu(etac)[P(OEt)$_3$]$_2$ as a precursor. The precursor produced free-standing copper nanowires on substrate surfaces at temperatures below 300 °C without recourse to templates or catalysts. The copper nanowires exhibited high purity and crystallinity with [111] orientation.

References

(1) Prober, D. E.; Feuer, M. D.; Giordano, N. *Appl. Phys. Lett.* **1980**, *37*, 94.
(2) Schnur, G.; Price, R.; Schoen, P.; Yager, P. *Thin Solid Films* **1987**, *152*, 181.
(3) Braun, E.; Eichen, Y.; Sivan, U.; Ben-Yoseph, G. *Nature* **1998**, *391*, 775.
(4) Yu, R.; Chen, L.; Liu, Q.; Lin, J.; Tan, K.; Ng, S.; Chan, H.; Xu, G.; Hor, T. *Chem. Mater.* **1998**, *10*, 718.
(5) Terrones, M.; Grobert, N.; Hsu, W.; Zhu, Y.; Hu, W.; Terrones, H.; Hare, J.; Kroto, H.; Walton, D. *MRS Bull.* **1999**, 44.
(6) Zach, M.; Ng, K.; Penner, R. *Science* **2000**, *290*, 2120.
(7) Al-Mawlawi, D.; Liu, C. Z.; Moskovits, M. *J. Mater. Res.* **1994**, *9*, 1014.
(8) Nishizava, M.; Menon, V. P.; Martin, C. R. *Science* **1995**, *268*, 700.
(9) Menon, V.; Martin, C. R. *Anal. Chem.* **1995**, *67*, 1920.
(10) Martin, C. R. *Chem. Mater.* **1996**, *8*, 1739.
(11) Wang, L.; Yu-Zhang, K.; Metrot, A.; Bonhomme, P.; Troyon, M. *Thin Solid Films* **1996**, *288*, 86.
(12) Martin, C. R.; Parthasarathy, R. V. *Adv. Mater.* **1995**, *7*, 487.
(13) Lakshmi, B. B.; Dorhout, P. K.; Martin, C. R. *Chem. Mater.* **1997**, *9*, 857.
(14) Han, Y.; Kim, J.; Stucky, G. *Chem. Mater.* **2000**, *12*, 2068.
(15) Thurn-Albrecht, T.; Schotter, J.; Kastle, G.; Emley, N.; Shibauchi, T.; Krusin-Elbaum, L.; Guarini, K.; Black, C.; Tuominen, M.;. Russell, T. *Science* **2000**, *290*, 2126.
(16) Song, J.; Wu, Y.; Messer, B.; Kind, H.; Yang, P. *J. Am. Chem. Soc.* **2001**, *123*, 10397.
(17) Schuchert, I. U.; Toimil Molares, M. E.; Dobrev, D.; Vetter, J.; Neumann, R.; Martin, M. *J. Electrochem. Soc.* **2003**, *150*, C189.
(18) Martin, B. R.; Dermody, D. J.; Reiss, B. D.; Fang, M., Lyon, L. A.; Natan, M. J.; Mallouk, T. E. *Adv. Mater.* **1999**, *11*, 1021.
(19) Pena, D.; Razavi, B.; Smith, P. A.; Mbindyo, J. K. N.; Natan, M. J.; Mayer, T. S.; Mallouk, T. E.; Keating, C. D. *Mater. Res. Soc. Symp. Proc.* **2001**, *636*, D4.6.1.
(20) Walter, E. C.; Murray, B. J.; Favier, F.; Kaltenpoth, G.; Grunze, M.; Penner, R. M. *J. Phys. Chem. B* **2002**, *44*, 11407.
(21) Choi, H.; Hwang, S. *Chem. Mater.* **1998**, *10*, 2326.
(22) Cu(etac)[P(OEt)$_3$]$_2$. ^{1}H NMR data (benzene-d_6, 400 MHz) δ 1.08 (−CCH$_3$), 1.12 (−CCH$_3$), 1.95 (−OCCH$_3$), 4.01 (POCH$_2$−), 4.07 (OCH$_2$−), 5.07 (−CCHC−); ^{13}C NMR data (benzene-d_6, 125.7 MHz) δ 188.0, 172.3, 82.2, 59.7, 57.8, 28.5, 16.7, 14.9; ^{31}P NMR data (benzene-d_6) δ 122.1. Anal. Calcd for C$_{18}$H$_{39}$CuO$_9$P$_2$: C, 41.2; H, 7.49; Found: C, 40.0; H, 7.42. Cu(etac)[P(OMe)$_3$]$_2$. ^{1}H NMR data (benzene-d_6) δ 1.05 (−CCH$_3$), 1.94 (−OCCH$_3$), 3.47 (POCH$_2$), 3.98 (−OCH$_2$−), 5.07 (−CCHC−); ^{31}P NMR data (benzene-d_6) δ 125.5. Cu(btac)[P(OMe)$_3$]$_2$. ^{1}H NMR data (benzene-d_6) δ 1.45 (−C(CH$_3$)$_3$), 1.97 (−CCH$_3$), 3.46 (OCH$_3$), 5.05 (−CCHC−); ^{31}P NMR data (benzene-d_6) δ 125.1. Cu(btac)-[P(OEt)$_3$]$_2$. ^{1}H NMR data (C$_6$D$_6$): δ1.12 (−CCH$_3$), 1.46 (−C(CH$_3$)$_3$), 1.94 (−CCH$_3$), 4.05 (OCH$_2$−), 5.00 (−CCHC−); ^{31}P NMR data (benzene-d_6) δ 122.1. Cu(btac)[P(OMe)$_3$][P(OEt)$_3$]. ^{1}H NMR data (benzene-d_6) δ 1.12 (−CCH$_3$), 1.45 (−C(CH$_3$)$_3$), 1.95 (−CCH$_3$), 3.47 (OCH$_3$), 4.03 (OCH$_2$−), 5.02 (−CCHC−); ^{31}P NMR data (benzene-d_6) δ 123.2.
(23) The Cu(I) complexes were distillable at around 120 °C/0.01 Torr except Cu(btac)[P(OMe)$_3$][P(OEt)$_3$] from which a mixture of Cu(btac)[P(OMe)$_3$]$_2$ and Cu(btac)[P(OEt)$_3$]$_2$ was collected. The Cu(I) complexes decomposed at 145−160 °C under N$_2$.

JA049217+