A Study on Synthesis of Micro/Nano Silver-Copper Core-Shell Powder with an Electric Conductivity of Silver

彭御賢、李清華

E-mail: 360088@mail.dyu.edu.tw

ABSTRACT

The purpose of this study is to fabricate the silver-copper core-shell powders with a comparable electric conductivity of silver. Silver-copper core-shell powders are copper powders coated with a thin layer of silver which have sizes less than 10 μm. They have the potential of replacing silver powders and can provide a new price-competitive material for electronic industry. In this study, the silver-copper core-shell powders were synthesized by the silver-copper co-reduction method and the copper electroless plating silver method.

In the silver-copper co-reduction method, reducing agents, molar ratios of metal – to-reducing agent, and adding points of the silver sulfate solution were chosen as the primary factors to fabricate silver-copper core-shell powders. The synthetic powders obtained by the silver-copper co-reduction method do not have silver-copper core-shell structure after analyzing by SEM. Also, its electric conductivity is too poor to be measured by the electric conductivity test. Therefore, powders which fabricated by silver-copper co-reduction method can not reach the goal of this research.

In the copper electroless plating silver method, silver-copper core-shell powders were fabricated in two stages. Pure copper powders were produced in the first stage and its optimal conditions which concluded by the Taguchi robust design method were: 21.5 kg of copper sulphate and 18.91 kg of phosphate were dissolved into 150 liters pure water at 70 °C and 300 RPM. The obtained copper powders have a average size of 7.36 μm. In the second stage, the obtained Cu powders will be subjected to electroless plating method to produce silver-copper core-shell powders. The optimal procedure found in this study were: (1) 2.53 g of Cu powders and 0.08 g of sodium citrate were dissolved into 100 ml pure water for copper powders dispersion, and (2) 1.17 g of silver sulphate and 0.065 g of sodium citrate were dissolved into 250 ml pure water for silver-salt solution, and (3) the silver-salt solution was fast added into copper dispersion under 1000 RPM for 10 min. The obtained optimal powders have a silver-copper core-shell structure which can be proved by using SEM and ESCA. Also, these powders have the same volume resistivity (1.43×10-4 Ω． cm) as pure silver powders when they are analyzed by electric conductivity test. The anti-oxidation property (0.1465 Wt%/min) of these powders is found to be significantly slower than pure copper (0.5745 Wt%/min) by TGA.

To conclude, the silver-copper core-shell powders with an electric conductivity of silver and good anti-oxidation properties can be successfully synthesized by the copper electroless plating silver method. The advantage is that their production costs are much cheaper than pure silver powders. Thus, they are suitable to replace silver in electronic conductivity material.

Keywords : Co-reduction、Electroless plating、Micron/Nano、Taguchi robust design,、Silver、Copper、Electric conductivity 、Core-shell

Table of Contents

目錄

圖目錄

表目錄

REFERENCES

1.宏鑫貴金屬有限公司，全球即時黃金價格，2011年8月30日，取自 http://www.ghx.com.tw/conpany.html，2011年。2.高濂、孫靜、?陽橋(2005)，奈米粉體的分散及表面改性，五南圖書出版股份有限公司，台北。3.陳敬中、劉劍洪(2006)，奈米材料科學導論，高等教育出版社，北京。4.莊萬發(1995)，超微粒子理論與應用，復漢出版社，台南。5.張邦維(2009)，奈米材料物理基礎，化學工業出版社，北京。6.彭御賢(2010)，化學合成法中?用纖維素作為分散劑合成微細銅粉之初探研究，科學與工程技術期刊，6(4)，47-57。7.楊育豪(2005)，廢DVD光碟片資源回收之研究，大葉大學環境工程研究所碩士論文。8.搜搜鋼電子商務網，半導體晶體生長, Retrieved 09 29, 2011, from http://baike.sososteel.com/doc/view/44359.html，2011年.9.銀冠國際有限公司，全球白銀Silver即時行情走勢圖，100年3月14日，取自 http://www.s-925.com/page18.htm，2011年。10.盧永坤(2005)，奈米科技概論，滄海書局，台中。11.蕭章能(2007)，以高分子分散劑作為?米粉體濕式分散研磨、界面改質及合成的研究，國?交通大學材料科學與工程系所博士?文。12.導電銀漿CPCA標準CPCA-4302(2004)，中國印製電路行業協會，北京。13.薛寬宏(2005)，奈米化學，頁，化學工業出版社，北京，49-57。14.簡長青(2007)，銅污泥資源化回收之研究，大葉大學環境工程研究所碩士論文。15.蘇品康(1989)，超微粒子材料技術，復漢出版社，台南。16.Ahlgren, M., Blomqvist, H. (2005). Influence of bias variation on residual stress and texture in TiAlN PVD coatings, Surface & Coatings Technology, 200: 157-160.17.Ansari, S. G., Ansari, Z. A., Wahab, R., Kim, Y. S., Khang, G., Shin, H. S. (2008). Glucose sensor based on nano-baskets of tin oxide templated in porous alumina by plasma enhanced CVD, Biosensors and Bioelectronics, 23: 1838-1842.18.Boukamp, B. A., Raming, T. P., Winnubst, A. J. A., Verweij, H. (2003). Electrochemical characterisation of 3Y-TZP – Fe2O3 composites, Solid State Ionics, 158: 381-394.19.Bi?er, M., ?i?man, ?. (2010). Controlled synthesis of copper nano-microstructures using ascorbic acid in aqueous CTAB solution. Powder Technology, 198(2):279-284.20.Ben-Moshe, T., Dror, I., Berkowitz, B. (2009). Oxidation of organic pollutants in aqueous solutions by nanosized copper oxide catalysts, Applied Catalysis B: Environmental, 85: 207-211.21.Bi, X. F., Ou, S. Q., Gong, S. K., Xu, H. B. (2002). Nano-crystallization and magnetic properties in the highly resistive Fe /Si /Zr /O ?lms prepared by EB-PVD, Materials Science and Engineering A, 344: 74-78.22.Chen, D. M., Liang, Z. C., Zhuang, L., Lin, Y. H., Shen, H. (2012). A novel method to achieve selective emitter for silicon solar cell using low cost pattern-able a-Si thin ?lms as the semi-transparent phosphorus diffusion barrier, Applied Energy, 92 315 – 321.23.Chattopadhyay, K., Dey, R., Ranu, B. C. (2009). Shape-dependent catalytic activity of copper oxide-supported Pd(0) nanoparticles for Suzuki and cyanation reactions, Tetrahedron Letters, 50: 3164-3167.24.Cioffi, N., Torsi, L., Ditaranto, N., Tantillo, G., Ghibelli, L., Sabbatini, L., Bleve-Zacheo, T., D ’ Alessio, M., Zambonin, P. G., Traversa, E. (2005). Copper Nanoparticle/Polymer Composites with Antifungal and Bacteriostatic Properties, Chemistry of materials, 17: 5255-5262.25.Choi, W. S., Kim, H. I., Kwak, S. S., Chung, H. Y., Chung, H. Y., Yamamoto, K., Oguchi, T., Tozuka, Y., Yonemochi, E., Terada, K. (2004). Amorphous ultrafine particle preparation for improvement of bioavailability of insoluble drugs: grinding characteristics of fine grinding mills, International Journal of Mineral Processing, 74S: S165-S172.26.Cheng, X., Zhang, X., Yin, H., Wang, A., Xu, Y. (2006). Modi?er effects on chemical reduction synthesis of nanostructured copper, Applied Surface Science, 253: 2727-2732.27.Chen, Y. J., Young, T. F., Lee, S. L., Huang, H. J., His, T. S., Chu, J. G., Jang, D. J. (2006). Electrochemical studies of nano-structured diamond thin-?lm electrodes grown by microwave plasma CVD, Vacuum, 80: 818-822.28.Dosbaeva, G. K., Veldhuis, S. C., Yamamoto, K., Wilkinson, D. S., Beake, B. D., Jenkins, N., Elfizy, A., Fox-Rabinovich, G. S. (2010). Oxide scales formation in nano-crystalline TiAlCrSiYN PVD coatings at elevated temperature, International Journal of Refractory Metals and Hard Materials, 28: 133-141.29.Darwin, J. D., Mohan Lal, D., Nagarajan, G. (2008). Optimization of cryogenic treatment to maximize the wear resistance of 18% Cr martensitic stainless steel by Taguchi method. Journal of Materials Processing Technology, 195(1-3): 241 – 247.30.Eshuis, A., Elderen, G. R. A. van, Koning, C. A. J. (1998). A descriptive model for the homogeneous precipitation of zinc sul?de from acidic zinc salt solutions, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 151: 505-512.31.Esteban-Cubillo, A., Pecharroma?n, C., Aguilar, E., Santare?n, J., Moya, J. S. (2006). Antibacterial activity of copper monodispersed nanoparticles into sepiolite, Journal of Materials Science, 41: 5208-5212.32.Egerton, R. F. (2005). Physical Principles of Electron Microscopy, Springer, 137. Canada.33.Esposito, S., Turco, M., Bagnasco, G., Cammarano, C., Pernice, P. (2011). New insight into the preparation of copper/zirconia catalysts by sol – gel method, Applied Catalysis A: General, 403: 128-135.34.Finny, E. E., Finke, R. G.. (2007). Nanocluster nucleation and growth kinetic and mechanistic studies: A review emphasizing transition-metal nanoclusters. Journal of Colloid and Interface Science, 317(2): 351-374.35.Fox-Rabinovich, G. S., Veldhuis, S. C., Scvortsov, V. N., Shuster, L. Sh., Dosbaeva, G. K., Migranov, M. S. (2004). Elastic and plastic work of indentation as a characteristic of wear behavior for cutting tools with nitride PVD coatings, Thin Solid Films, 469-470: 505-512.36.Fox-Rabinovich, G. S., Weatherly, G. C., Dodonov, A. I., Kovalev, A. I., Shuster, L. S., Veldhuis, S. C., Dosbaeva, G. K., Wainstein, D. L., Migranov, M. S. (2004 a). Nano-crystalline filtered arc deposited (FAD) TiAlN PVD coatings for high-speed machining applications, Surface and Coatings Technology, 177-178: 800-811.37.Fox-Rabinovich, Yamamoto, G. S., K., Veldhuis, S. C., Kovalev, A. I., Shuster, L. S., Ning, L. (2006). Self-adaptive wear behavior of nano-multilayered TiAlCrN/WN coatings under severe machining conditions, Surface & Coatings Technology, 201: 1852-1860.38.Fox-Rabinovich, G. S., Yamamoto, K., Aguirre, M. H., Cahill, D. G., Veldhuis, S. C., Biksa, A., Dosbaeva, G., Shuster, L. S. (2010). Multi-functional nano-multilayered AlTiN/Cu PVD coating for machining of Inconel, Surface & Coatings Technology, 204: 2465-2471.39.Gutie?rrez-Wing, C., Pe?rez-Herna?ndez, R., Mondrago?n-Galicia, G., Villa-Sa?nchez, G., Ferna?ndez-Garc??a, M. E., Arenas-Alatorre, J., Mendoza-Anaya, D. (2009). Synthesis of silica-silver wires by a sol-gel technique, Solid State Sciences, 11: 1722-1729.40.Goia, D. V., Matijevic, E. (1998). Preparation of monodispersed metal particles, New Journal of Chemistry, 22: 1203-1215.41.Grieve, K., Mulvaney, Grieser, P., F. (2000). Synthesis and electronic properties of semiconductor nanoparticles/quantum dots, Current Opinion in Colloid & Interface

Science, 5: 168-172.42.Goto, T., Masumoto, H., Niizuma, M. (2002). Low temperature oxidation of CVD SiC by electron cyclotron resonance plasma, Materials Chemistry and Physics, 75: 235-240.43.Huang, C. Y., Sheen, S. R. (1997). Synthesis of nanocrystalline and monodispersed copper particles of uniform spherical shape, Materials Letters, 30: 357-361.44.Hu, M., Zhou, K., Wang, C., Xu, R. (2008). Cl- induced synthesis of submicron cubic copper particles in solution, Journal of University of Science and Technology Beijing, 15(5): 659-664.45.Hiemenz, P. C. (1986). Principle of colloid and surface chemistry, second edition, Marcel Dekker, New York.46.Jang, B. K., Matsubara, H. (2005). In?uence of rotation speed on microstructure and thermal conductivity of nano-porous zirconia layers fabricated by EB-PVD, Scripta Materialia, 52: 553-558.47.Jang, B. K., Matsubara, H. (2005 a). Hardness and Young ' s modulus of nanoporous EB-PVD YSZ coatings by nanoindentation, Journal of Alloys and Compounds, 402: 237-241.48.Jakubowska, M., Jarosz, M., Kie?basinski, K. (2011). A. M?o?niak, New conductive thick-?lm paste based on silver nanopowder for high power and high temperature applications, Microelectronics Reliability, 51: 1235 – 1240.49.Jesurani, S., Kanagesan, S., Velmurugan, R., Thirupathi, C., Sivakumar, M., Kalaivani, T. (2011). Nanoparticles of the giant dielectric material, calcium copper titanate from a sol-gel technique, Materials Letters, 65: 3305-3308.50.Jiang, X., Trunov, M. A., Schoenitz, M., Dave, R. N., Dreizin, E. L. (2009). Mechanical alloying and reactive milling in a high energy planetary mill, Journal of Alloys and Compounds, 478: 246-251.51.Kumar, A., Singh, P., Saxena, A., De, A., Chandra, R., Mozumdar, S. (2004). Nano-sized copper as an ef?cient catalyst for one pot three component synthesis of thiazolidine-2,4-dione derivatives, Catalysis Communications, 10: 17-22.52.Kim, K. D., Han, D. N., Kim, H. T. (2004). Optimization of experimental conditions based on the Taguchi robust design for the formation of nano-sized silver particles by chemical reduction method. Chemical Engineering Journal, 104(1-3): 55-61.53.Kim, K. D., Kim, S. H., Kim, H.T. (2005). Applying the Taguchi method to the optimization for the synthesis of TiO2 nanoparticles by hydrolysis of TEOT in micelles. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 254(1-3): 99-105.54.Kawashita, M., Tsuneyama, S., Miyaji, F., Kokubo, T., Kozuka, H., Yamamoto, K. (2000). Antibacterial silver-containing silica glass prepared by sol-gel method, Biomaterials, 21: 393-398.55.Knite, M., Teteris, V., Kiploka, A. (2003). The effect of plasticizing agent on strain-induced change of electric resistivity of carbon – polyisoprene nano-composites, Materials Science and Engineering C, 23: 787-790.56.Kra?mer, M., Schmidt, T., Sto?we, K., Maier, W. F. (2006). Structural and catalytic aspects of sol – gel derived copper manganese oxides as low-temperature CO oxidation catalyst, Applied Catalysis A: General, 302: 257-263.57.Kim, Y., Lee, B., Yang, S., Byun, I., Jeong, I., Cho, S. M. (2012). Use of copper ink for fabricatin g conductive electrodes and RFID antenna tags by screen printing, Current Applied Physics, 12: 473-478.58.Lee, B., Kim, Y., Yang, S., Jeong, I., Moon, J. (2009). A low-cure-temperature copper nano ink for highly conductive printed electrodes, Current Applied Physics, 9: e157-e160.59.Lee, C. L., Chang, K. C., Syu, C. M. (2011). Silver nanoplates as inkjet ink particles for metallization at a low baking temperature of 100°C, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 381: 85-91.60.Lu, C. Y., Wey, M. Y., Fu, Y.H. (2008). The size, shape, and dispersion of active sites on AC-supported copper nanocatalysts with polyol process: The effect of precursors, Applied Catalysis A: General, 344: 36-44.61.Lewis, J. A. (2000). Colloidal Processing of Ceramics, Journal of the American Ceramic Society, 83(10): 2341-59.62.Lee, J. S., Kim, J. K., Kim, M. S., Kang, N., Lee, J. H. (2011). Reliability of flip-chip bonded RFID die using anisotropic conductive paste hybrid material, Transactions of Nonferrous Metals Society of China, 21: s175-s181.63.London metal exchange, LME Copper, Retrieved March 14, 2011 from http://www.lme.com/copper.asp, 2011.64.LaMer, V. K., Dinegar, R. H. (1950). Theory, Production and Mechanism of Formation of Monodispersed Hydrosols, Journal of the American Chemical Society, 72: 4847-4854.65.LaMer, V. K. (1952). Nucleation in phase transitions, Industry & Engineering Chemistry, 44: 1270.66.Liu, X. W., Lin, J. H., Hsieh, W. J., Shih, H. C. (2002). Morphology and characterization of highly nitrogenated, aligned, amorphous carbon nano-rods formed on an alumina template by ECR-CVD, Diamond and Related Materials, 11: 1193-1199.67.Lin, Y. H., Lin, H. D., Liu, C. K., Huang, M. W., Chen, J. R., Shih, H. C. (2010). Structure and characterization of the multilayered Ti-DLC ?lms by FCVA, Diamond & Related Materials, 19: 1034-1039.68.Lee, Y., J. Choi, R., Lee, K. J., Stott, N. E., Kim, D.(2008). Large-scale synthesis of copper nanoparticles by chemically controlled reduction for applications of inkjet-printed electronics, Nanotechnology, 19: 415604.69.Meunier, C., Munnik, F., Stauffer, J., Germann, E., Mikhailov, S. (2005). Dual FCVA – PECVD deposition for DLC films, Thin Solid Films, 482: 197-200.70.Muraviev, D. N., Macana?s, J., Parrondo, J., Mun?oz, M., Alonso, A., Alegre, S., Ortueta, M., Mijangos, F. (2007). Cation-exchange membrane as nanoreactor: Intermatrix synthesis of platinum-copper core-shell nanoparticles, Reactive & Functional Polymers, 67: 1612-1621.71.Ma, D., Ma, S., Xu, K. (2005). The tribological and structural characterization of nano-structured Ti – Si – N ?lms coated by pulsed-d.c. plasma enhanced CVD, Vacuum, 79: 7-13.72.Matijevic, E. (2007). Nanosize Precursors as Building Blocks for Monodispersed Colloids, Colloid Journal, 69 (1): 29-38.73.Mazen, F., Baron, T., Papon, A. M., Truche, R., Hartmann, J. M. (2003). A two steps CVD process for the growth of silicon nano-crystals, Applied Surface Science, 214: 359-363.74.Maata, H. ter, Hogendoorn, J.A., Versteeg, G.F. (2005). The removal of hydrogen sul?de from gas streams using an aqueous metal sulfate absorbent Part II. The regeneration of copper sul?de to copper oxide—an experimental study, Separation and Puri?cation Technology, 43: 199-213.75.Murray J. L. (1984). Calculations and stable of metastable equilibrium diagrams of the Ag-Cu and Cd-Zn systems, Metallurgical and Materials Transactions A, 15: 261-268.76.Moffit, M., Eisenberg, A. (1995). Size control of nanoparticles in semiconductor-polymer composites. 1. control via multiplet aggregation numbers in styrene-based random ionomers, Chemical Material, 7: 1178-1184.77.McCann, R., Roy, S. S., Papakonstantinou, P., Abbas, G., McLaughlin, J. A. (2005). The effect of thickness and arc current on the structural properties of FCVA synthesised ta-C and ta-C:N films, Diamond & Related Materials, 14: 983-988.78.Mitra, S., Sridharan, K., Unnam, J., Ghosh, K. (2008). Synthesis of nanometal oxides and nanometals using hot-wire and thermal CVD, Thin Solid Films, 516: 798-802.79.Matsumura, Y., Ishibe, H. (2009). Selective steam reforming of methanol over silica-supported copper catalyst prepared by sol-gel method, Applied Catalysis B: Environmental, 86: 114-120.80.Nara, K. E., Yamatokoriyama, N. F., Akashi, S. W., Higashiosaka, H. M., Ikeda, T. T. (1988). Comductive copper paste composition, US Patent, No.4789411.81.Ney, C., Kohlmann, H., Kickelbick, G. (2011). Metal hydride synthesis through reactive milling of metals with solid acids in a planetary ball mill, International Journal of Hydrogen Energy, 36: 9086-9090.82.Pourbaix, M. (1974). Atlas of Electrochemical Equilibria in Aqueous Solutions, NACE and Cebelcor, Utah.83.Pham, L. Q., Sohn, J. H., Kim, C. W., Park, J. H., Kang, H. S., Lee, B. C., Kang, Y. S. (2012). Copper nanoparticles incorporated with conducting polymer: Effects of copper concentration and surfactants on the stability and conductivity, Journal of Colloid and Interface Science, 365 103 – 109.84.P?rvulescu, V. I., Cojocaru, B., P?rvulescu, V., Richards, R., Li, Z., Cadigan, C., Granger, P., Miquel, P., Hardacre, C. (2010) Sol-gel-entrapped nano silver catalysts-correlation between active silver species and catalytic behavior, Journal of Catalysis, 272: 92-100.85.Park, W. J., Choe, J., Lee, S. M., Lee, H. J., Lee, J., Song, K. H., Lee, H. (2011). N-heterocyclic carbene – silver complexes: Potential conductive materials for silver pastes in electronic applications, Polyhedron, 30: 465 – 469.86.Rashid, A., Landstr?m, L., Brodoceanu, D., Piglmayer, K. (2009). Lamp-assisted CVD of carbon micro/nano-structures using metal catalysts and CH2I2 precursor, Applied Surface Science, 255: 5368-5372.87.Roucoux, A., Schulz, J., Patin, H. (2002). Reduced Transition Metal Colloids: A Novel Family of Reusable Catalysts?, Chem. Rev., 102: 3757-3778.88.Reisfeld, R. , Saraidarov, T. (2006). Innovative materials based on sol-gel technology, Optical Materials, 28: 64-70.89.Raming, T. P., Winnubst, A. J. A., Kats, C. M. van, Philipse, A. P. (2002). The Synthesis and Magnetic Properties of Nanosized Hematite (α -Fe2O3) Particles, Journal of Colloid and Interface Science, 249: 346-350.90.Raming, T. P., Winnubst, A. J. A., Zyl, W. E. van, Verweij, H. (2003). Densi?cation of zirconia-hematite nanopowders, Journal of the European Ceramic Society, 23: 1053-1060.91.Ruparelia, J. P., Chatterjee, A. K., Duttagupta, S. P., Mukherji, S. (2008). Strain speci?city in antimicrobial activity of silver and copper nanoparticles, Acta Biomaterialia, 4: 707-716.92.Rahaman, M. N. (2007). Ceramic Processing, Taylor & Francis, USA.93.Schulz, D. L., Curtis, C. J., Ginley, D. S. (2001). Surface Chemistry of Copper Nanoparticles and Direct Spray Printing of Hybrid Particle/Metallorganic Inks, Electrochemical and Solid-State Letters, 4(8): C58-C61.94.Shaw D. J. (1992). Introduction to colloid and surface chemistry, forth edition, Butterworth-Heinemann, Oxford.95.Sheeja, D., Tay, B. K., Sze, J. Y., Yu, L. J., Lau, S. P. (2003). A comparative study between pure and Al-containing amorphous carbon films prepared by FCVA technique together with high substrate pulse biasing, Diamond and Related Materials, 12: 2032-2036.96.Suarez, M. A., Grosjean, T., Charraut, D., Courjon, D. (2007). Nanoring as a magnetic or electric field sensitive nano-antenna for near-field optics applications, Optical Communications, 270: 447-454.97.Singh, M., Sinha, I., Singh, A. K., Mandal, R.K. (2011). LSPR and SAXS studies of starch stabilized Ag – Cu alloy nanoparticles, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 384: 668-674.98.Sarkar, S., Jana, A.D., Samanta, S.K., Mostafa, G. (2007). Facile synthesis of silver nano particles with highly efficient anti-microbial property, Polyhedron, 26: 4419-4426.99.Sim, S. M., Chen, B. J., Sun, X. W. (2004), In situ resistance measurement during FCVA deposition of ZnO thin ?lms, Ceramics International, 30: 2019-2022.100.Tu, C. H., Wang, A. Q., Zheng, M. Y., Wang, X. D., Zhang, T. (2006). Factors in?uencing the catalytic activity of SBA-15-supported copper nanoparticles in CO oxidation, Applied Catalysis A: General, 297: 40-47.101.Tang, L., Du, P., Han, G., Weng, W., Zhao, G. (2003). Preparation of silver dispersed PbTiO3 ?lm by sol-gel method, Materials Science and Engineering B, 99: 370-373.102.Tsuji, M., Hikino, S., Tanabe, R., Matsunaga, M., Sano, Y. (2010). Syntheses of Ag/Cu alloy and Ag/Cu alloy core Cu shell nanoparticles using a polyol method, crystal engineering, 12: 3900-3908.103.Takeno, N. (2005). Atlas of Eh-pH diagrams, National Institute of Advanced Industrial Science and Technology, Japan.104.Wang, H., He, Y. l., Gao, W. D., Li, J., Gu, L. I., Wang, Y. Y. (2008). Antibacterial properties of PLA nonwovens deposited with nanostructured silver film, Journal of Textile Research, 29(6): 52-55.105.Wang, J., Ito, T. (2007). Improved field emission characteristics of nano-structured carbon films deposited on polycrystalline CVD diamond, Diamond & Related Materials, 16: 364-368.106.Wang, J., Ito, T. (2007 a). CVD growth and field emission characteristics of nano-structured films composed of vertically standing and mutually intersecting nano-carbon sheets, Diamond & Related Materials, 16: 589-593.107.Wang, P., Wang, X., Chen, Y., Zhang, G., Liu, W., Zhang, J. (2007). The effect of applied negative bias voltage on the structure of Ti-doped a-C:H ?lms deposited by FCVA, Applied Surface Science, 253: 3722-3726.108.Wu, S.P. (2006). Preparation of ultra-fine copper powder and its lead-free conductive thick film, Materials Letters, 61: 3526-3530.109.Wu, S.P., Meng, S. (2006 a). Preparation of micron size copper powder with chemical reduction method, Materials Letters, 60: 2438-2442.110.Wu, S.P. (2007). Preparation of fine copper powder using ascorbic acid as reducing agent and its application in MLCC, Materials Letters, 61: 1125-1129.111.Wu, S.P., Ni, J., Jiao, L., Zeng, Z. (2007 a). Preparation of ultra-?ne copper – nickel bimetallic powders with hydrothermal – reduction method, Materials Chemistry and Physics, 105: 71-75.112.Wu, S.P., Gao, R.Y., Xu, L.H. (2009). Preparation of micron-sized ?ake copper powder for base-metal-electrode multi-layer ceramic capacitor, Journal of Materials Processing Technology, 209: 1129-1133.113.Wikipedia, the free encyclopedia, Copper, Retrieved Augest 30, 2011 from http://en.wikipedia.org/wiki/Copper, 2011.114.Wikipedia, the free encyclopedia, Silver, Retrieved Augest 30, 2011 from http://en.wikipedia.org/wiki/Silver, 2011.115.Wang, X. Y., Liu, S. Q., Huang, K. L., Feng, Q. J., Ye, D. L., Liu, B., Liu, J. L., Jin, G. H. (2010). Fixation of CO2 by electrocatalytic reduction to synthesis of dimethyl carbonate in ionic liquid using effective silver-coated nanoporous copper composites, Chinese Chemical Letters, 21: 987-990.116.Xie, S. Y., Ma, Z. J., Wang, C. F., Lin, S. C., Jiang, Z. Y., Huang, R. B., Zheng, L. S. (2004). Preparation and self-assembly of copper nanoparticles via discharge of copper rod electrodes in a surfactant solution: a combination of physical and chemical processes, Journal of Solid State Chemistry, 177: 3743-3747.117.Xu, S. l., Song, X. Y., Fan, C. H., Chen, G. Z., Zhao, W., You, T., Sun S. X. (2007). Kinetically controlled synthesis of Cu2O microcrystals with various morphologies by adjusting pH value, Journal of Crystal Growth, 305: 3-7.118.Yu, D., Wang, D., Yu, W., Qian, Y. (2003). Synthesis of ITO nanowires and nanorods with corundum structure by a co-precipitation-anneal method, Materials Letters, 58: 84-87.119.Yang, G., Yu, L., Chen, X., Zhang, P. (2009). Hydrophobic surfaces of spin-assisted layer-by-layer assembled polyelectrolyte multilayers doped with copper nanoparticles and modi?ed by ?uoroalkylsilane, Applied Surface Science, 255: 4097-4101.120.Yang, J. G., Zhou, Y. l., Takeshi, O., Ryoichi, I., Masazumi, O. (2007). A new method for preparing hydrophobic nano-copper powders, Journal of Material Science, 42: 7638-7642.121.Yoshiya, M., Wada, K., Jang, B. K., Matsubara, H. (2004) Computer simulation of nano-pore formation in EB-PVD thermal barrier coatings, Surface & Coatings Technology, 187: 399-407.122.Yan, M., Ying, H. G., Ma, T. Y. (2008). Improved microhardness and wear resistance of the as-deposited electroless Ni-P coating. Surface & Coatings Technology, 172: 5909-5913.123.Yonezawa, T., Nishida, N., Hyono, A. (2010). One-pot Preparation of Antioxidized Copper Fine Particles with a Unique Structure by Chemical Reduction at Room Temperature, Chemistry Letters, 39, 548-549.124.Yang, W. H., Tarng, Y. S. (1998). Design optimization of cutting parameters for turning operations based on the Taguchi method. Journal of Materials Processing Technology, 84(1-3): 122-129.125.Yu, W., Xie, H. Q., Chen, L. F., Li, Y., Zhang, C., (2010). Controlled synthesis of narrow-dispersed copper nanoparticles. Journal of Dispersion Science and Technology, 31: 364 – 367.126.Yang, Z. H., Zhang, D. P., Zhang, W. X., Chen, M. (2009). Controlled synthesis of cuprous oxide nanosphe res and copper sul?de hollow nanospheres, Journal of Physics and Chemistry of Solids, 70: 840-846.127.Zhao, B, Liu, Z., Zhang, Z., Hu, L. (1997). Improvement of Oxidation Resistance of Ultrafine Copper Powders by Phosphating Treatment, Journal of solid state chemistry, 130: 157-160.128.Zhang, L., Wang, H. Z., Li, J. G. (2009). Solution reduction synthesis and characterizations of HCP Co nanoplatelets. Materials Chemistry and Physics, 116(2-3): 514-518.129.Zheng, X., Wang, S., Wang, S., Zhang, S., Huang, W., Wu, S. (2004). Copper oxide catalysts supported on ceria for low-temperat ure CO oxidation, Catalysis Communications, 5: 729-732.130.Zhang, X., Yin, H., Cheng, X., Hu, H., Yu, Q., Wang, A. (2006). Effects of various polyoxyethylene sorbitan monooils (Tweens) and sodium dodecyl sulfate on re?ux synthesis of copper nanoparticles, Materials Research Bulletin, 41: 2041-2048.