



PERGAMON

Solid State Communications 125 (2003) 365–368

solid
state
communications

www.elsevier.com/locate/ssc

Growth of self-assembled copper nanostructure on conducting polymer by electrodeposition

D.K. Sarkar, X.J. Zhou, A. Tannous, M. Louie, K.T. Leung*

Department of Chemistry, University of Waterloo, 200 University Ave West, Waterloo, Ont., Canada N2L 3G1

Received 18 October 2002; received in revised form 10 December 2002; accepted 12 December 2002 by D.J. Lockwood

Abstract

In the present work, self-assembled nanostructures of copper are grown by electrodeposition on a thin conducting polymer (polypyrrole) film electropolymerized on a gold electrode. The shapes, sizes and the densities of the nanostructures are found to depend on the thickness of the polypyrrole thin film, which provides an easy means to control the morphology of these nanostructures. In particular, for the same applied potential on the gold electrode, smaller nanocrystals with a higher density are observed on thinner polymer films while bigger nanocrystals at a lower density are found on thicker films.

© 2003 Elsevier Science Ltd. All rights reserved.

PACS: 82.45; 61.46; 72.80.L; 73.61.P

Keywords: A. Conducting polymers; A. Nanocrystals; D. Electrodeposition

The generation of nanostructured materials on a surface is a new thrust in materials science due to the continuing miniaturization of electronic and mechanical devices. In general, feature sizes 30–300 nm and larger are routinely produced by electron-beam and photolithography techniques, respectively. Important progress has been made over the past few years in the preparation of ordered ensembles of metal and semiconductor nanocrystals to fabricate feature size less than 30 nm [1,2]. Devices fabricated entirely from polymers are now available, opening up the possibility of adapting polymer processing technologies to fabricate inexpensive, large-area devices using non-lithographic techniques [3,4]. Nanostructured materials have attracted much recent attention due to their important roles in many technological areas such as heterogeneous catalysis [5], photonics [6], single electron and quantum devices [7]. The development of nanotechnology requires good understanding of the evolution of the shape, size and distribution of nanoparticles in different growth processes [8,9]. Nanoparticles have been commonly grown in physical [10,11] and

electrochemical processes [12–16]. In the physical deposition process, the deposition rate and surface diffusion coefficient determine the shape, size and density of the nanoparticles on a specific substrate surface [17]. On the other hand, the concentration and pH of the electrolyte as well as the applied potential all play a prominent role in the electrochemical deposition process [18]. The use of an STM tip to develop copper nanostructures on a single-crystal gold electrode electrochemically has also been demonstrated [19]. Two common growth modes can be defined either as progressive or instantaneous, in the electrochemical deposition process, depending on the surface energies of the substrate and the deposited materials as well as their interface energy. In the Volmer–Weber growth process, the growth mode is instantaneous due to the large difference in the surface energies of the substrate and the deposited material [20]. The number of active nucleation sites is proportional to the applied potential because the nucleation barrier becomes lower with increasing applied potential [21].

Organic conducting polymers, particularly in the form of thin films, are attractive candidates for microelectronic applications [22,23] due to their unique combination of electrical, mechanical and physical properties. Furthermore,

* Corresponding author. Tel.: +1-519-888-4567x5826; fax: +1-519-746-0435.

E-mail address: tong@uwaterloo.ca (K.T. Leung).

self-assembly of metal nanostructures on diblock polymer substrate by making use of different wetting properties of the polymers has been demonstrated [24,25]. In this work we report the growth of self-assembled Cu nanostructures and the control of their growth morphology by simply varying the thickness of the polypyrrole film. Our goal is to incorporate nanostructured materials into conducting polymers for the development of next generation semiconducting and optical devices.

In the present work, polypyrrole was deposited on a gold electrode by electrochemical polymerization at an applied potential of 800 mV (versus AgCl/Ag standard potential) in a solution of 0.05 M pyrrole and 0.1 M NaClO₄. By controlling the amount of total charge transferred, we could vary the thickness of the polypyrrole film from 25 to 500 nm. Copper was then deposited electrochemically on the polypyrrole film (of different thicknesses) in a solution of 0.01 M CuSO₄ and 0.1 M NaClO₄ under different applied potential from –400 to –1400 mV (versus AgCl/Ag standard potential). For a fixed applied potential, the amount of deposited copper atoms could be similarly varied from 0.05 to 6.5 equivalent monolayer (ML) by controlling the amount of charge. (One ML of Cu atoms on Cu(100) plane is equivalent to 1.6×10^{16} atoms/cm².) We present the deposition results of ~5 ML of copper on polypyrrole films with different thicknesses obtained at an applied potential of –1000 mV. Scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) have been used to examine, respectively, the surface morphology and chemical interaction of the copper nanocrystals deposited on the polypyrrole films.

The most exciting result is the control of the size and density of the copper nanocrystals by simply changing the thickness of the polymer film. The electric field at the surface of a dielectric film can be reduced with increasing film thickness. For example, the electric field at the surface of a self-assembled monolayer of n-alkyl thiols (4×10^4 V/cm) has been shown to be weaker than that at the interface (3×10^5 V/cm) on a gold electrode at an applied potential of 1 V [26]. The SEM micrograph shown in Fig. 1 illustrates the dramatic effect of a non-uniform polypyrrole film on the growth morphology of the copper nanoparticles. Evidently, two distinct coverage regions of copper nanocrystals (with different sizes and number densities) can be identified. Since polypyrrole has similar dielectric properties as a semiconductor [27,28], the difference in the film thickness can produce different electric fields at the polypyrrole surface [26]. The higher potential at the surface of the thinner part of the polymer film (Region A) leads to the creation of more nucleation sites and therefore a higher density of nanocrystals, while the opposite is true for the thicker part (Region B). The nanocrystals on the thinner part are also notably smaller than those on the thicker part. Closer examination of the copper nanostructure (over the entire film substrate) reveals evidence of nanostructure organization into a ‘ribbon-like’

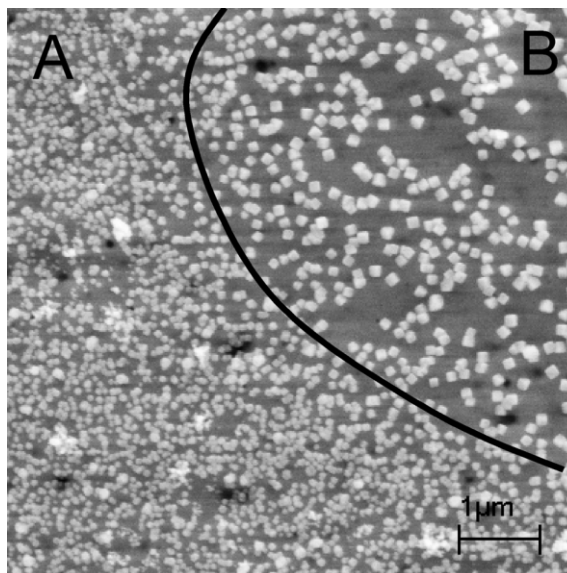


Fig. 1. SEM micrograph of an overview of morphology of copper nanoparticles on a $10 \mu\text{m} \times 10 \mu\text{m}$ area of a polypyrrole film with non-uniform thickness. A smaller film thickness gives rise to a higher surface potential and hence a larger number of nucleation sites (Region A). On the other hand, the surface potential of a thicker film is correspondingly lower, which leads to less nucleation sites (Region B). Some evidence of Cu nanostructures self-organizing along certain morphological features of the underlying polymer surface is also observed.

pattern, which may correlate with the underlying physical features of the polymer substrate.

Fig. 2 more clearly demonstrates the important role of the film thickness of the polymer substrate in controlling the average size and number density of the copper nanocrystals on the polymer film. An equal amount of charge (0.01 C) has been used for the copper deposition at a constant applied potential of –1000 mV on a 6-mm-diameter cylindrical gold electrode. As shown in Fig. 2(a), a nearly uniform two-dimensional copper film interspersed with a few nanoscale islands is observed on the bare gold electrode surface (i.e. before any polypyrrole film deposition). For a 25-nm-thick polypyrrole film, we observe in Fig. 2(b) the initial formation of three-dimensional copper nanoparticles partially covered by one-dimensional metallic nanowires (not shown). These irregularly shaped nanoparticles are seen to evolve into better-defined three-dimensional nanocrystals as the thickness of the substrate polypyrrole film is increased to a critical value. Furthermore, the size of the nanocrystals has evidently increased with increasing film thickness, e.g., from 90 nm on a 100-nm-thick polypyrrole film (Fig. 2(c)) to 105 nm on a 200-nm-thick film (Fig. 2(d)), while the corresponding number density of the nanocrystals has reduced concomitantly.

Fig. 3 summarizes the changes in the size and number density of the copper nanocrystals as a function of the film

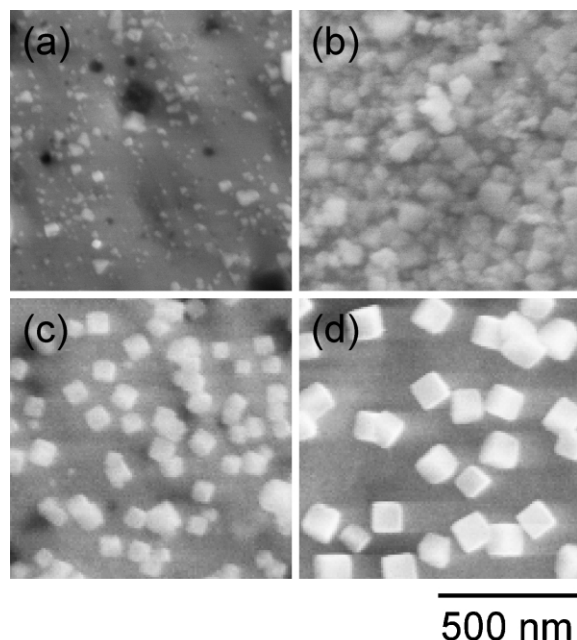


Fig. 2. SEM micrograph of the copper nanostructure on a gold electrode (a) without and with predeposition of (b) 25 nm, (c) 100 nm and (d) 200 nm thick polypyrrole films.

thickness of the polypyrrole substrate. The experimental data has been fitted semiempirically with the following function:

$$N = 10^8(8.5 + 5.7 \exp(-(d - 50)/71)), \quad (1)$$

which illustrates that the number density of the nanocrystals per cm^2 , N , depends on the film thickness of the polymer in nm, d , in an exponential fashion. On the other hand, the size of the nanocrystals L (in nm) follows a linear dependence on the thickness as:

$$L = 78 + 0.13d \quad (2)$$

While the average size of the nanocrystals increases from 86 nm on a 50-nm-thick polymer film to 105 nm on a 200-nm-thick film, a reciprocal reduction in the number density from $\sim 1.4 \times 10^9 \text{ cm}^{-2}$ for the 50-nm-thick film to $0.9 \times 10^9 \text{ cm}^{-2}$ for the 200-nm-thick film is clearly evident. The morphological changes of the copper nanocrystals on the polypyrrole film are consistent with an instantaneous growth process, which arises due to the weak interaction and the large difference in the surface energy between the copper atoms and the polymer substrate [10]. The current transient profiles (not shown) also support an instantaneous growth picture. Furthermore, the N 1s XPS spectra (not shown) show a reduction in the intensity ratio of the pyrrolic N ($-\text{NH}-$) peak (at 399.6 eV) to the iminic N ($-\text{C}=\text{N}-$) peak (at 397.7 eV) from 6.2 for bare polypyrrole to 1.6 upon copper nanocrystals deposition, which confirms the copper interaction with the pyrrolic N component of the polypyrrole

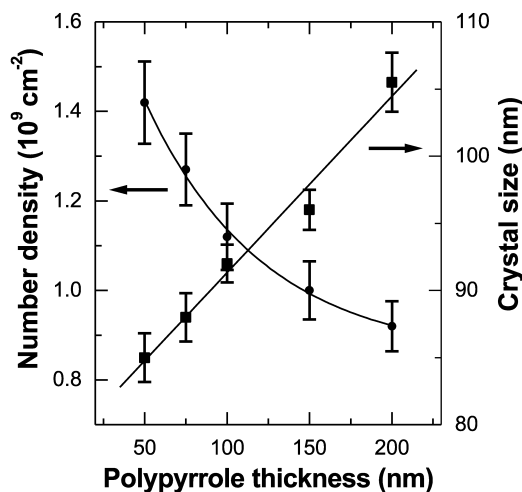


Fig. 3. Correlation of the size of the copper nanocrystals and their surface number density with the film thickness of the polypyrrole film.

film. This N 1s intensity ratio reverts to the polypyrrole case upon sputtering the copper-nanostructured polypyrrole surface. The tendency of forming Cu–N bond is not very strong due to the poor solubility of N in copper. Copper ions arriving on the surface of polypyrrole become copper atoms upon reduction by two electrons from the polypyrrole. The number of nucleation sites generally depends on the surface energy of polypyrrole, the surface energy of copper, the concentration of the solvent and the applied potential on the working electrode. For a constant applied potential, the number of nucleation sites on a polypyrrole film of a given film thickness is correspondingly predetermined. Copper atoms on the polymer surface can undergo surface diffusion to other already grown copper clusters due to the weak bonding between Cu and N in polypyrrole (relative to the Cu-to-Cu bonds). In the absence of strong perturbation from the polymer surface, the copper atoms diffuse freely on the surface and nucleate into a cubic shape conforming to its natural fcc crystal structure.

In summary, we demonstrate that the growth morphology of copper nanocrystals at a thin polypyrrole film can be easily controlled by varying the thickness of the polymer film and hence the effective electric field at the polymer surface. Reduction of the surface electric field increases the effective nucleation barrier, which in turn reduces the number of nucleation sites. The present work also illustrates an inverse correlation between the number density of the nanocrystals and their average size with increasing film thickness. Some evidence of ordering of the copper nanocrystals along certain morphological features of the polypyrrole film has also been observed, though further investigations are necessary to quantify these correlations. These growth features all point to the intricate nucleation mechanism of copper atoms on a thin polypyrrole film under the influence of the surface electric field.

Acknowledgements

This work was supported by the Natural Sciences and Engineering Research Council of Canada.

References

- [1] C.J. Kiely, J. Fink, M. Brust, D. Bethell, D.J. Schiffrin, Spontaneous ordering of bimodal ensembles of nanoscopic gold clusters, *Nature* 396 (1998) 444.
- [2] C.A. Mirkin, R.L. Letsinger, R.C. Mucic, J.J. Storhoff, DNA based method for rationally assembling nanoparticles into macroscopic materials, *Nature* 382 (1996) 607.
- [3] R.H. Friend, R.W. Gymer, A.B. Holmes, J.H. Burroughes, R.N. Marks, C. Taliani, D.D.C. Bradley, D.A. Dos Santos, J.L. Brédas, M. Lögdlund, W.R. Salaneck, Electroluminescence in conjugated polymers, *Nature* 397 (1999) 121.
- [4] R.F. Service, Patterning electronics on the cheap, *Science* 278 (1997) 383.
- [5] R. Shima, Y. Chakk, M. Folman, A. Hoffman, F. Lai, S. Praver, Role of embedded titanium nanoparticles for enhanced chemical vapor deposition diamond formation on silicon, *J. Vac. Sci. Technol. B* 17 (1999) 1912.
- [6] Z. Wang, C.T. Chan, W. Zhang, N. Ming, P. Sheng, Three dimensional self-assembly of metal nanoparticles: possible photonic crystal with a complete gap below the plasma frequency, *Phys. Rev. B* 64 (2001) 113108.
- [7] S. Bandyopadhyay, Self-assembled nanoelectronic quantum computer based on the Rashba effect in quantum dot, *Phys. Rev. B* 61 (2000) 13813.
- [8] M.J. Yacaman, J.A. Ascencio, H.B. Liu, J.G. Torresdey, Structure shape and stability of nanometric sized particles, *J. Vac. Sci. Technol. B* 19 (2001) 1091.
- [9] L.D. Mark, Experimental studies of small particle structures, *Rep. Prog. Phys.* 57 (1994) 603.
- [10] D.H. Cole, K.R. Shull, L.E. Rehn, P. Baldo, Metal–polymer interaction in polymer/metal nanocomposite, *Phys. Rev. Lett.* 78 (1997) 5006.
- [11] B. Fischer, H. Brune, J.V. Barth, A. Fricke, K. Kern, Nucleation kinetics on inhomogeneous substrates: Al/Au(111), *Phys. Rev. Lett.* 82 (1999) 1732.
- [12] C. Ji, G. Oskam, P.C. Searson, Electrochemical nucleation and growth of copper on Si(111), *Surf. Sci.* 492 (2001) 115.
- [13] R. Schuster, V. Kirchner, X.H. Xia, A.M. Bittner, G. Ertl, Nanoscale electrochemistry, *Phys. Rev. Lett.* 80 (1998) 5599.
- [14] S. Morin, A. Lachenwitzer, O.M. Magnussen, R.J. Behm, Potential-controlled step flow to 3D step decoration transition: Ni electrodeposition on Ag(111), *Phys. Rev. Lett.* 83 (1999) 5066.
- [15] K. Sieradzki, S.R. Brankovic, N. Dimitrov, Electrochemical defect-mediated thin film growth, *Science* 284 (1999) 138.
- [16] S. Strbac, O.M. Magnussen, R.J. Behm, Nanoscale pattern formation during electrodeposition: Ru on reconstructed Au(111), *Phys. Rev. Lett.* 83 (1999) 3246.
- [17] H. Brune, Microscopic view of epitaxial metal growth: nucleation and aggregation, *Surf. Sci. Rep.* 31 (1998) 121.
- [18] H. Natter, R. Hempelmann, Nanocrystalline copper by pulsed electrodeposition: the effect of organic additives, bath temperature and pH, *J. Phys. Chem.* 100 (1996) 19525.
- [19] D.M. Kolb, R. Ullmann, T. Will, Nanofabrication of small copper clusters on Gold (111) electrodes by scanning tunnelling microscope, *Science* 275 (1997) 1097.
- [20] R. Krumm, B. Guel, C. Schmitz, G. Staikov, Nucleation and growth in electrodeposition of metals on n-Si(111), *Electrochim. Acta* 45 (2000) 3255.
- [21] B. Scharifker, G. Hills, Theoretical and experimental studies of multiple nucleation, *Electrochim. Acta* 28 (1983) 879.
- [22] I.E. Vermeir, N.Y. Kim, P.E. Laibinis, Electrical properties of covalently linked silicon/polypyrrole junctions, *Appl. Phys. Lett.* 74 (1999) 3860.
- [23] M.C. Lonergan, A tunable diode based on an inorganic semiconductor conjugated polymer interface, *Science* 278 (1997) 2103.
- [24] W.L. Lopes, H.M. Jaeger, Hierarchical self-assembly of metal nanostructures on diblock copolymer scaffolds, *Nature* 414 (2001) 735.
- [25] A.M. Higgins, R.A.L. Jones, Anisotropic spinodal dewetting as a route of self-assembly of patterned surfaces, *Nature* 404 (2000) 476.
- [26] J.N. Pope, D.A. Buttry, Measurements of the potential dependence of electric field magnitudes at an electrode using fluorescent probes in a self-assembled monolayer, *J. Electroanal. Chem.* 498 (2001) 75.
- [27] R. Singh, A.K. Narula, Correlation between dielectric relaxation and d.c. electrical conduction in polypyrrole family of polymers, *Synth. Met.* 82 (1996) 245.
- [28] V.N. Prigodin, A.J. Epstein, Nature of insulator–metal transition and novel mechanism of charge transport in the metallic state of highly doped electronic polymers, *Synth. Met.* 125 (2002) 43.