Directed Molecular Self-Assembly:
Its Applications to Potential Electronic Materials

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Self-assembly techniques are becoming excellent substitutes for conventional photolithographic techniques in terms of the feature sizes of the patterned structures. In particular, this technique can offer the benefits of a bottom-up strategy for material fabrication. Self-assembly of two- and three-dimensional structures on the nanometer scale from a large variety of potential electronic materials has been achieved using the diverse physical and chemical forces between molecules, nanoparticles and substrate surfaces. The fabrication of nano- and/or micro-electronic devices utilizing a molecular-level self-assembly process appears more promising than ever before due to radical advances in synthesis and processing techniques that allow unprecedented control of the formation and manipulation of the nanomaterial into the desired device structures. In this review, recent efforts in the synthesis and processing of novel materials based on surface and molecular forces acting during the self-assembly of the materials and structures are briefly introduced. This review clearly shows that the directed molecular self-assembly will become a core technology that can serve as an indication of the unimaginable electronic devices in the near future.

Keywords: self-assembly, surface forces, electronic materials, bottom-up strategy

1. INTRODUCTION

The physicochemical properties of nano-sized materials are truly unique, novel, and sometimes even tunable while such properties are missing in the bulk phase. For instance, quantum confinement phenomena allow semiconductor nanoparticles to undergo a widening of their bandgap energy as the particle size becomes smaller, thereby resulting in blue-shifts in the optical spectra [1, 2] and a change in their energy density from continuous to discrete energy levels as the transition moves from the bulk to the nanoscale quantum dot state [3]. In addition, interesting electrical properties including resonance tunneling and Coulomb blockade effects [4-6] are observed with metallic and semiconducting nanoparticles, and endohedral fullerenes and carbon nanotubes can be processed to exhibit a tunable bandgap of either metallic or semiconducting properties [7-9]. These very different phenomena are mainly due to larger surface area-to-volume ratio at the nanoscale compared to the bulk. Thus, the surface forces become more important when the nano-sized materials exhibit unique optical or electrical properties. The surface (or molecular) forces can be generally categorized as electrostatic, hydration (hydrophobic, and hydrophilic), van der Waals, capillary forces, and direct chemical interactions. Based on these forces, the synthesis and processing techniques of these interesting nano-sized materials have been well established as capable of producing high-quality monodisperse nanocrystals of numerous semiconducting and metallic materials, fullerenes of varying properties, single- and multi-wall carbon nanotubes, conducting polymers, and other nano-sized systems. The next key step in the application of these materials to device fabrication is undoubtedly the formation of sub-nanoelements into functional and desired nanostructures without mutual aggregation. To achieve the goal of innovative developments in the areas of microelectronic, optoelectronic and photonic devices with unique physical and chemical characteristics of the nano-sized materials, it may be necessary to immobilize these materials on surfaces and/or assemble them into an organized network.

Many significant advances in one- to three-dimensional arrangements in nanoscale have been achieved using what is known as the 'bottom-up' approach. Unlike typical top-down photolithographic approaches, the bottom-up process offers numerous attractive advantages, including the realization of molecular-scale feature sizes, the potential of three-dimensional assembly and an economical mass fabrication process [10]. Self-assembly is one of the few vital techniques available for controlling the orchestration of nanostructures

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via this bottom-up technology. The self-assembly process is defined as the autonomous organization of components into well-organized structures. It can be characterized by its numerous benefits; it is cost-effective, versatile, facile, and the process seeks the thermodynamic minima of a system, resulting in stable and robust structures[11]. As the description suggests, it is a process in which defects are not energetically favored, thus the degree of perfect organization is relatively high [12, 13]. As described earlier, there are various types of interaction forces by which the self-assembly of molecules and nanoparticles can be accomplished. In this review, via the directed self-assembly of these forces, the types of potential electronic materials that have been successfully developed thus far are introduced.

2. ELECTROSTATIC SELF-ASSEMBLY

The process characterized by electrostatic interactions between nanoparticles or molecules is one of most popular methods by which self-assembly processes occur. This method was first proposed by Iler in 1966[14], who reported the innovative technique of building multilayer films composed of positively and negatively charged colloidal particles, such as silica and alumina. The technical significance of this original process became known only after the 1990s when Decher[15] revived the concept and reported the fabrication of multilayer polymeric thin films composed of oppositely charged polyelectrolytes. Since then, this approach has been
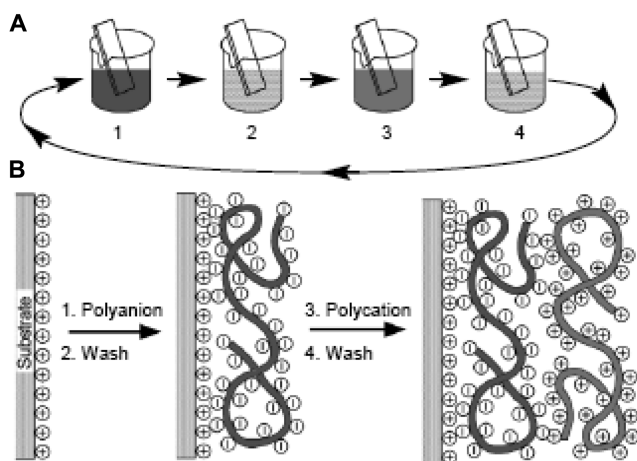
exploited by a numerous research groups who have worked to achieve optically, magnetically and electrically distinctive nano-sized materials composed of metals, semiconductors, magnetic materials, molecular dyes and polymers[16-19]. The oppositely charged species are bonded together by strong electrostatic forces, forming uniform, robust and stable films[15]. The ESA process is governed by the adsorption and desorption equilibria in cationic and anionic solutions, and the film deposition involves simple immersion, rinse and dry steps in a cyclic manner, as shown in Fig. 1. The thickness of the polyelectrolyte species can be tuned with the degree of ionization, or more simply, the solution pH[20].

One example of such nanocomposite thin films composed of coinage nanoparticles was presented by Kumar *et al.*[21], in which amine-derivatized gold (positive surface charge) and the carboxylic acid-derivatized silver colloidal particles (negative surface charge) were deposited layer by layer sequentially. The effective charging of gold and silver colloidal particles was accomplished by the self-assembly of 4-aminothiophenol and 4-carboxythiophenol molecules on the colloidal particle surfaces, respectively, and by subsequently ionizing the terminal groups to $-NH_3^+$ and $-COO$ at a suitable solution pH. The fabrication process consisted of simple substrate immersions into the two colloidal solutions in an alternating fashion, along with rinsing and drying steps in between, which are common in any layer-by-layer self-assembly process from a solution. A schematic of this build-up process is shown in Fig. 2. Additionally, similar nanocomposite thin films of colloidal particles and polyelectrolytes were fabricated and characterized by many other groups[22–25].

The layer-by-layer electrostatic self-assembly can also be applied to polymeric and other organic molecules, including conjugated conducting polymers[26], dendrimers[27], chromophoric and electrooptic polymers[28, 29]. This ESA process has shown the versatility of incorporating a wide range of materials into the formation of self-healing molecular-level
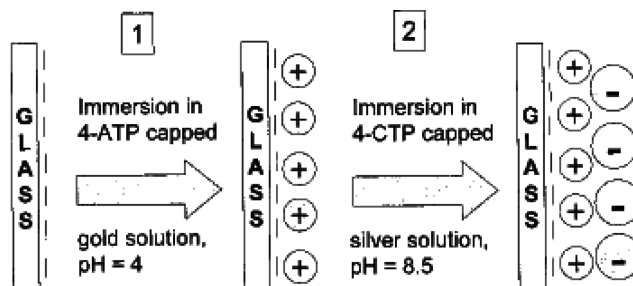

Fig. 1. (A) Schematic of the film deposition process using slides and beakers: Steps 1 and 3 represent the adsorption of a polyanion and polycation, respectively, and steps 2 and 4 are washing steps. The four steps are the basic buildup sequence for the simplest film architecture, (A/B)*n*. The construction of more complex film architecture types requires only additional beakers and a different deposition sequence. (B) Simplified molecular picture of the first two adsorption steps, depicting film deposition starting with a positively charged substrate: Counterions are omitted for clarity. The polyion conformation and layer interpenetration are an idealization of the surface charge reversal with each adsorption step[15].

Fig. 2. Formation of electrostatically assembled alternating layers of gold and silver colloidal particles on glass substrates: Step 1: self-assembly of positively charged gold particles on negatively charged glass during immersion in 4-ATP-capped gold solution at pH) 4. Step 2: self-assembly of negatively charged silver particles on gold-coated glass during immersion in 4-CTP-capped silver solution at pH) 8.5[21].

functional thin films. Clearly, the ESA process has been actively employed in the fabrication of diverse nano-structured devices such as non-linear optics, chemical sensors and flexible displays.

3. CHEMICAL SELF-ASSEMBLY

Chemical (or covalent) bonding is the most attractive mode in the self-assembly of molecules and nanoclusters, as it is far more specific in terms of grasping functional groups. It yields very stable, robust and permanent structures. In contrast, electrostatic self-assembly generally shows a lack of orientation of the functional groups[30]. Chemical self-assembly typically offers a method in which energetically very stable self-assembled films can be prepared. This method of self-assembly was first introduced by Sagiv[31], and it is based on the chemisorption of monomers, polymers and semiconducting and metallic moieties onto specific substrates. For example, Jonas et al. at the Université Catholique de Louvain[32, 33] grew polymer films by alternating the chemisorption of polymer and reactive dyes. Other types of composite thin films containing monomeric linker molecules bridging inorganic nanoparticles originated from the concept of SAMs. This concept involves the spontaneous formation of tightly arranged monolayers upon immersion of a substrate into an appropriate solution. It is commonly carried out with oxide-bearing substrates with organosilanes or coinage metal substrates with alkanethiols[34]. Via the careful selection of terminal groups tethered on organosilanes and alkanethiols, it is possible to functionalize the SAM surface for further manipulation. For example, Kim *et al.*[35,36] recently reported a conducting polythiophene thin film that was chemically self-assembled on a functionalized silane SAM surface. This process is a good example of directed chemical self-assembly of thiophene monomers immediately polymerized on an amino-functionalized silane SAM surface. Via the directed chemical self-assembly technique, polythiophene thin films were highly selectively deposited and robustly adhered to an aminosilane SAM pre-patterned silicon oxide substrate, as shown in Fig. 3.

Lee *et al.*[37] recently investigated the chemical self-assembly of a Cu thin film on a silicon oxide substrate using an iodine-catalyzed chemical vapor deposition method. They employed bifunctional organosilane molecules, $HS-(CH_2)_3-Si(OCH_3)_3$, in which the thiol group had an affinity for a copper while the silane groups preferentially bonded to SiO_2 via covalence. In this method, bifunctional molecules were first adsorbed onto a bare oxide substrate to form a SAM, on which a Cu film was subsequently grown. This self-assembly method was intended to improve the adhesion of copper electrodes to a bare oxide substrate via the bifunctional SAM. Similarly, Sarathy *et al.*[38] demonstrated a layer-by-layer fabrication of a nanoparticle–molecular spacer sandwich-type structure into superlattices using dithiols, metal and semiconducting nanoparticles. Through molecular engineering and prudent selection of functional spacers/surfactants, it is possible to promote molecular level self-assembly through covalent bonding.

4. SURFACE FORCE-INDUCED SELF ASSEMBLY

Here, surface forces can be categorized as relatively weak forces exhibited by various types of surfaces. These can include hydration, van der Waals, and capillary forces. Surface forces can be used directly as pathways by which molecules or nanoparticles are self-assembled. For example, solvent evaporation in a controlled manner can bring colloids together into an ordered array, just as surfactants can form regularly arranged structures[39, 40]. In addition, nanotemplates can be obtained directly utilizing microphase separation of block copolymers at various concentrations based on the immiscibility of two-polymer blocks[41]. With respect to the former method, nanoparticles and other molecules can self-assemble in the presence of a thin liquid layer when the thickness of this layer is suitably controlled. For colloids, it has been hypothesized that particles are assem-
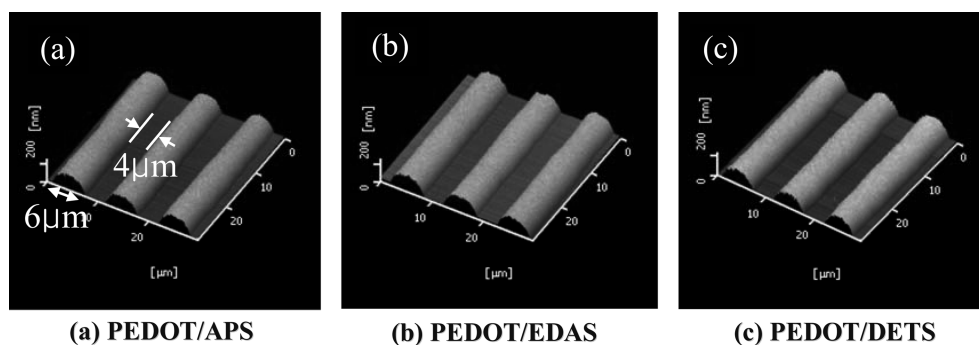

(a) PEDOT/APS   **(b) PEDOT/EDAS**   **(c) PEDOT/DETS**

Fig. 3. An oxidized silicon wafer substrate was micro-contact printed with n-octadecyltrichlorosilane (OTS) monolayer. Subsequently, its negative pattern was self-assembled with three different amino-functionalized alkylsilanes, (3-aminopropyl)trimethoxysilane (APS), N-(2-aminoethyl)-3-aminopropyltrimethoxy silane (EDAS), and (3-trimethoxysilylpropyl) diethylenetriamine (DETS). Poly(3,4-ethylenedioxythiophene) (PEDOT) nanofilms were then highly selectively grown on the aminosilane pre-patterned areas via a vapor phase polymerization method[35, 36].
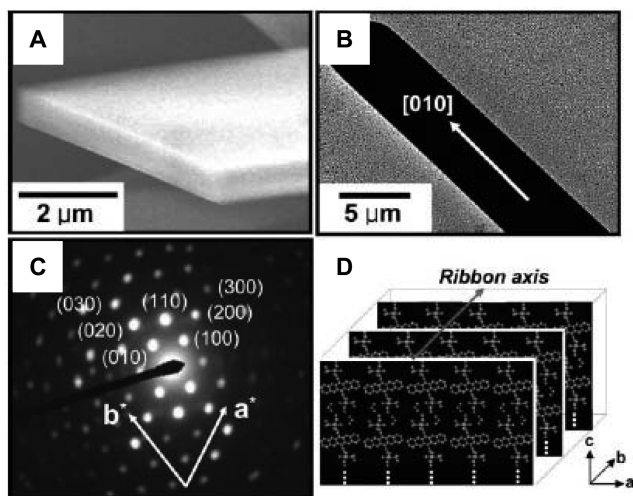
Fig. 4. Morphological features and structure characterization of 1D single-crystalline TIPS-PEN microribbons: A) SEM image of a TIPS-PEN microribbon formed on a silicon substrate showing a rectangular cross-section of the microribbon with well-defined facets. B) Transmission electron microscopy (TEM) image of TIPS-PEN microribbons on a silicon nitride window, showing preferential growth along the [010] direction. C) Selected-area electron diffraction (SAED) pattern of a TIPS-PEN microribbon. D) Schematic representation of the self-assembly of TIPSPEN molecules into a single-crystalline microribbon grown along the direction of the p–p stacking [43].

Fig. 5. Patterned crystallization: (a) $LiClO_4$, crystallized from a saturated solution of methanol that formed on the hydrophilic (SAM formed from $HS(CH_2)_{15}COOH$) regions of a patterned substrate. The hydrophobic regions were formed by rubber stamping the adsorption of $HS(CH_2)_{15}CH_3$. (b, c) Arrays of crystals of $CuSO_4$ that formed on hydrophilic regions from 1 M, aqueous solutions [45].

bled either by the convective flow at the boundary of the array or by the attractive capillary force acting between particles due to surface tension at the film surface [42].

Some examples of molecular self-assembly are governed purely by van der Waals force. Its products are sometimes perfectly ordered single-crystal structures. Cho *et al.*[43] recently demonstrated that functionalized pentacene molecules can self-assemble and form a perfect single crystal through a solvent exchange method in the solution phase. Clearly, this process is predominantly governed by the van der Waals force between the molecules. This is a typical example of a structure-directed molecular self-assembly process. Specifically, two identical and bulky functional groups bonded to the center of a pentacene molecule effectively serves to promote more intimate π-π bonding between the molecules, thereby resulting in 1-D crystalline microribbons. An organic field-effect transistor based on this type of microribbon can then be fabricated; this development has been shown to exhibit excellent performance, showing a high mobility of ca. $1.42 cm^2 V^{-1} s^{-1}$ and an on/off ratio of ca. 10^{5} [43]. Figure 4 shows the morphological features and structure characterization of 1-D single-crystalline TIPS-PEN (Triisopropylsilylethynyl Pentacene) microribbons.

Another form of interaction for mediating self-assembly processes involve hydration forces (hydrophilic and hydrophobic interactions), for example, exploiting the hydrophobic and/or hydrophilic interactions on surfactant molecules coating CdSe quantum dots. Chen *et al.*[44] demonstrated a
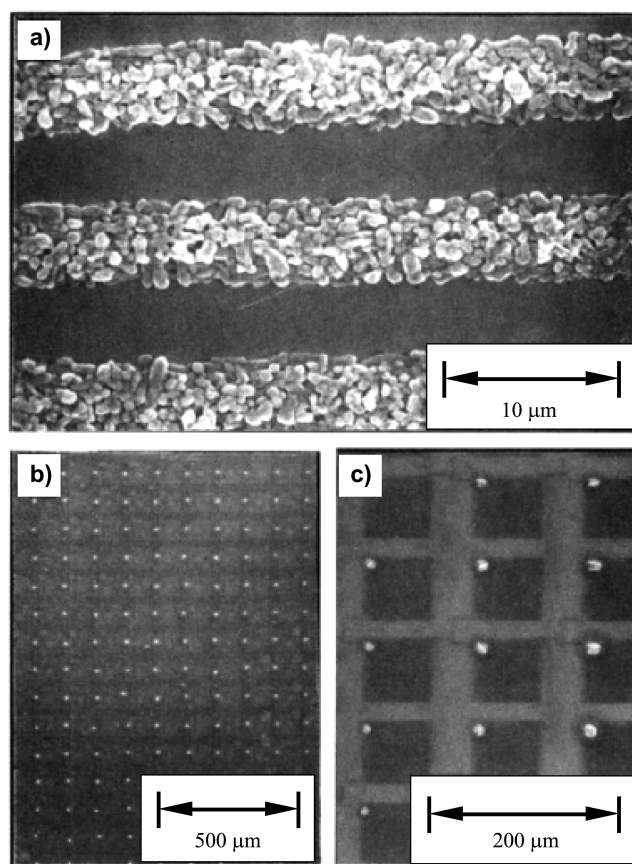
low temperature, cost-effective and simple process of constructing patterned SAMs. The wettability of nanocrystals was determined by the terminal functionality of surfactant molecules that were tethered to the nanocrystal surface. In this process, hydrophobic surfactant-capped nanocrystals were obtained by derivatizing CdSe dots with tri-*n*-octylphosphine oxide, and hydrophilic counterparts were derived from 4-mercaptobenzoic acid. A pattern on a gold substrate defining hydrophilic and hydrophobic regions was accomplished via microcontact printing of SAMs[45] with different alkanethiolates, specifically 1-dodecanethiol and 16-mercaptohexadecanoic acid. The presence of quantum dots as well as inorganic crystals on the expected region was visually confirmed by atomic force and optical microscopic imaging (see Fig. 5).

5. OTHER COMBINED TECHNIQUES

Micropatterning is currently an essential process in the

PDMS stamp

(a) OTS inking

(b) Amino silane dip-coating

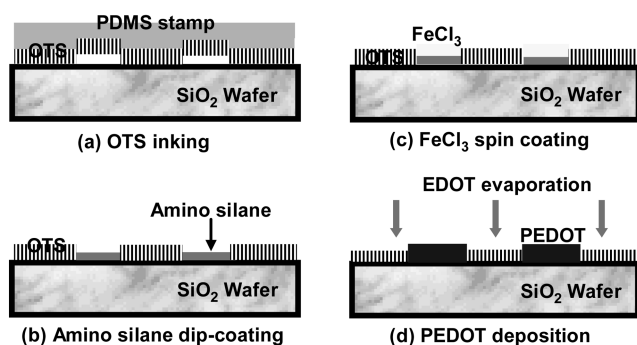**(c) FeCl₃ spin coating**

(d) PEDOT deposition

Fig. 6. The overall procedure for the patterning of a polythiophene nanofilm on an aminosilane/OTS mixed SAM surface: As shown, this procedure employs four different self-assembly techniques in a row (OTS microcontact printing, aminosilane dip-coating, hydrophilic wetting of FeCl₃, and *in-situ* polymerization of EDOT (chemical self-assembly)) [51].

microelectronics and optoelectronics industry. In particular, photolithography is the most popular tool capable of mass-producing patterned structures with feature sizes as small as 100 nm [46]. Unlike conventional photolithography, advanced lithographic techniques are realized with extreme UV, soft x-ray, electron beam and focused ion beams to achieve dimensions smaller than 100 nm. However, they come with numerous challenges; it is an expensive technology that is not suitable for nonplanar surfaces. In addition, it only allows two-dimensional microstructures, and the restrictive nature of the photoresist is a further issue [47, 48]. A revolutionary alternative method was introduced by Whitesides et al. at Harvard [49] termed soft lithography. It uses a patterned elastomer as a stamp, mold or mask to generate the desired micropatterns. This represents a unique method of printing that utilizes self-assembly to form micropatterns and microstructures with different materials [50]. As it operates under the principle of self-assembly, the equilibrated final structure tends to prevent defects and provides the lowest energy form. SAMs exhibit many attractive characteristics, such as ease of fabrication, few defects, and ambient processing conditions. Currently, countless examples exist of micropatterning processes that employ more than two self-assembly techniques, including a microcontact printing method. A very recent example reported by Kim *et al.*[35,51] is the micropatterning process of polythiophene thin films using a combination of microcontact printing, hydrophilic wetting of FeCl₃, and vapor-phase polymerization (chemical self-assembly) methods. Figure 6 shows the overall procedure for the patterning of a poly(3,4-ethylenedioxythiophene) nanofilm on an aminosilane/n-octadecyl trichlorosilane (OTS) mixed SAM surface. The aforementioned authors also measured the electrical conductivity of the polythiophene film and found it to be as high as ~600 S/cm, which is acceptable for it serve as an electrode for an organic field effect transistor [51]. In addition to this example, it is not surprising that most very

recently developed patterning processes employ two or more self-assembly techniques, including various soft lithographic methods [52-54].

CONCLUSION

From numerous application examples mentioned, it has been shown that the self-assembly technique is an excellent substitute for conventional photolithographic technology in terms of the feature sizes of patterned structures. In addition, this technique can offer the benefit of a bottom-up strategy for material fabrication. The self-assembly of two- and three-dimensional structures on the nanometer scale from a large variety of electronic materials is being realized by diverse physical and chemical forces between molecules, nanoparticles, and substrate surfaces. The fabrication of nano- and/or micro-electronic devices utilizing molecular-level self-assembly processes appear more promising than ever before due to the radical advances in synthesis and processing techniques that allow unprecedented control in terms of the nanomaterial formation and manipulation into desired device structures. Taking advantage of established chemistry and physics, a sensible selection of molecules and nanoclusters that function as conductors, semiconductors or insulators can potentially lead to novel applications and device realization, particularly in micro/optoelectronics. Many technical hurdles lie ahead, however, especially in terms of the design and preparation of novel materials and structures with precisely controlled geometry. In the near future, it is clear that directed molecular self-assembly processes will play an essential role in the overcoming of these hurdles.

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REFERENCES

1. A. A. Seraphin, E. Werwa, and K. D. Kolenbrander, *J. Mater. Res.* **12**, 3386 (1997).
2. C. B. Murray, D. J. Norris, and M. G. Bawendi, *J. Am. Chem. Soc.* **115**, 8706 (1993).
3. A. D. Yoffe, *Adv. Phys.* **42**, 173 (1993).
4. K. K. Likharev, *Proc. IEEE* **87**, 606 (1999).
5. D. Goldhaber-Gordon, M. S. Montemerlo, J. C. Love, G. J. Opiteck, and J. C. Ellenbogen, *Proc. IEEE* **85**, 521 (1997).
6. U. Simon and G. Schon, Electrical properties of chemically tailored nanoparticles and their applications in microelectronics, *Handbook of Nanostructured Materials and Nanotechnology* **3**, Academic, New York (2000).
7. S. Stevenson, G. Rice, T. Glass, K. Harich, F. Cromer, M. R. Jordan, J. Craft, E. Hadju, R. Bible, M. M. Olmstead, K.

Maitra, A. J. Fisher, A. L. Balch, and H. C. Dorn, *Nature* **401**, 55 (1999).

8. N. Hamada, S. Sawada, and A. Oshiyama, 1992 *Phys. Rev. Lett.* **68**, 1579 (1992).

9. K. Harigaya, *Phys. Rev. B* **60**, 1452 (1999).

10. M. Brust and C. J. Kiely, *Colloids Surf. A* **202**, 175 (2002).

11. G. M. Whitesides and B. Grzybowski, *Science* **295**, 2418 (2002).

12. G. M. Whitesides, J. P. Mathias, and C. T. Seto, 1991 *Science* **254**, 1312 (1991).

13. J. S. Lindsey, *New J. Chem.* **15**, 153 (1991).

14. R. K. Iler, *J. Colloid Interface Sci.* **21**, 569 (1966).

15. G. Decher, *Science* **277**, 1232 (1997).

16. F. Aliev, M. Correa-Duarte, A. Mamedov, J. W. Ostrander, M.Giersig, L. Liz-Marzan, and N. Kotov, *Adv. Mater.* **11**, 1006 (1999).

17. W. Shrof, S. Rozouvan, E. Vankeuren, D. Horn, J. Schmitt, and G. Decher, *Adv. Mater.* **10**, 338 (1998).

18. F. Caruso, R. A. Caruso, and H. Mohnwald, *Science* **282**, 1111 (1998).

19. M. Gao, C. Lesser, S. Kirstein, H. Mohwald, A. L. Rogach, and H. Weller, *J. Appl. Phys.* **87**, 2297 (2000).

20. A. A. Antipov, G. B. Sukhorukov, E. Donath, and H. Mohwald, *J. Phys. Chem. B* **105**, 2281 (2001).

21. A. Kumar, A. B. Mandale, and M. Sastry, *Langmuir* **16**, 6921 (2000).

22. J. Schmitt and G. Decher, *Adv. Mater.* **9**, 61 (1997).

23. J. F. Hicks, Y. Seok-Shon, and R. W. Murray, *Langmuir* **18**, 2288 (2000).

24. Y. J. Liu, A. Rosidian, K. Lenahan, Y. X. Wang, T. Y. Zeng, and R. O. Claus, *Smart Mater. Struct.* **8**, 100 (1999).

25. A. A. Mamedov, A. Belov, M. Giersig, N. N. Mamedova, and N. A. Kotov, *J. Am. Chem. Soc.* **123**, 7738 (2001).

26. T. Yamaue, T. Kawai, M. Onoda, and K. Yoshino, *J. Appl. Phys.* **85**, 1626 (1999).

27. V. N. Bliznyuk, F. Rinderspacher, and V. V. Tsukruk, *Polymer* **39**, 5249 (1998).

28. J-A. He, K. Yang, J. Kumar, S. K. Tripathy, L. A. Samuelson, T. Oshikiri, H. Katagi, H. Kasai, S. Okada, H. Oikawa, and H. Nakanashi, *J. Phys. Chem. B* **103**, 11050 (1999).

29. T. Zeng, R. O. Claus, F. Zhang, W. Du, and K. L. Cooper, *Smart Mater. Struct.* **10**, 780 (2001).

30. P. Bertrand, A. Jonas, A. Laschewsky, and R. Legras, *Macromol. Rapid Commun.* **21**, 319 (2000).

31. L. Netzer and J. Sagiv, *J. Am. Chem. Soc.* **105**, 674 (1983).

32. M. Koetse, A. Kotzev, A. Laschewsky, and A. M. Jonas, *Mater. Sci. Eng. C* **18**, 239 (2001).

33. M. Koetse, A. Laschewsky, A. M. Jonas, and T. Verbiest, *Colloids Surf. A* **198–200**, 275 (2002).

34. A. Ulman, *An Introduction to Ultrathin Organic Films: From Langmuir–Blodgett to Self-Assembly*, Academic, Boston, MA (1991).

35. S. Kim, I. Pang, and J. Lee, *Macromol. Rapid Commun.* **28**, 1574 (2007).

36. I. Pang, S. Kim, and J. Lee, *Surf. Coat. Technol.* **201**, 9426 (2007).

37. H. J. Park, H. J. Shin, H. S. Jung, C. Kim, M. M. Sung, C. M. Lee, H. S. Soh, and J. G. Lee, *Surf. Coat. Technol.* **201**, 9432 (2007).

38. K. V. Sarathy, P. J. Thomas, G. U. Kulkarni, and C. N. R. Rao, *J. Phys. Chem. B* **103**, 399 (1999).

39. C. J. Brinker, Y. Lu, A. Sellinger, and H. Fan, *Adv. Mater.* **11**, 579 (1999).

40. M. Li, H. Schnablegger, and S. Mann, *Nature* **402**, 393 (1999).

41. T. Thurn-Albrecht, R. Steiner, J. DeRouchey, C. M. Stafford, E. Huang, M. Bal, M. Tuominen, C. J. Hawker, and T. P. Russell, *Adv. Mater.* **12**, 787 (2000).

42. K. Nagayama, *Colloids Surf. A* **109**, 363 (1996).

43. D. H. Kim, D. Y. Lee, H. S. Lee, W. H. Lee, Y. H. Kim, J. I. Han, and K. Cho, *Adv. Mater.* **19**, 678 (2007).

44. C-C. Chen, C-P. Yet, H-N. Wang, and C-Y. Chao, *Langmuir* **15**, 6845 (1999).

45. A. Kumar, H. A. Biebuyck, and G. M. Whitesides, *Langmuir* **10**, 1498 (1994).

46. M. D. Levenson, *Semicond. Sci. Technol.* **10**, 57 (1995).

47. P. Rai-Choudhury, (ed) *Handbook of Microlithography Macromachining and Microfabrication* **1**, SPIE Optical Engineering Press, Bellingham, WA (1997).

48. R. D. Miller and G. M. Wallraff, *Adv. Mater. Opt. Electron.* **4**, 95 (1994).

49. X-M. Zhao, Y. Xia, and G. M. Whitesides, *J. Mater. Chem.* **7**, 1069 (1997).

50. Y. Xia and G. M. Whitesides, *Annu. Rev. Mater. Sci.* **28**, 153 (1998).

51. I. Pang, S. Kim, and J. Lee, *J. Nanosci. Nanotechnol.* in press (2007).

52. R. D. Piner, J. Zhu, F. Xu, S. H. Hong, and C. A. Mirkin, *Science* **283,** 661 (1999).

53. Ivanisevic and C. A. Mirkin, *J. Am. Chem. Soc.* **123**, 7887 (2001).

54. C. A. Mirkin, *Inorg. Chem.* **39**, 2258 (2000).