Fabrication of Highly Ordered Multilayer Films Using a Spin Self-Assembly Method**

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Ultrathin multilayer films have attracted much interest because of their wide applications as sensors, integrated optics, friction-reducing coatings, biological surfaces, light-emitting devices (LEDs), or surface-orientation layers.[1–5] Most of these applications require preparation of stable and well-organized films with fast fabrication processes. Several years ago, Decher et al.[6] described a layer-by-layer self-assembly (SA) method for the fabrication of multilayer thin films consisting of anionic and cationic polymer layers. This layer-by-layer SA method is principally based on the self-diffusion process in which charged polyelectrolyte chains are adsorbed onto an oppositely charged surface owing to the electrostatic attraction. As a result, adsorption time, proper control of pH, polyelectrolyte concentration, and amount of added ionic salt should be considered in order to increase the surface coverage of a polymer layer adsorbing onto a substrate. In addition, without thorough washing using a flow of pure solvent after the adsorption of a polyelectrolyte layer, the weakly adsorbed polyelectrolyte chains significantly increase the surface roughness of the multilayer films, yielding poor film quality. Consequently, optimum conditions for both adsorption and careful washing steps are required to prepare well- defined multilayer films.

In this communication, we describe a *spin self-assembly method* as an alternative for making well-organized multilayer films in a very short process time. Poly(allylamine hydrochloride) (PAH) and poly(sodium 4-styrenesulfonate) (PSS) were, for example, used as the cationic and anionic polymers, respectively. Inorganic cadmium sulfide (CdS) nanoparticles carrying negative charges at the particle surface were also used to demonstrate the quality of the internal structure of multilayer films prepared by the spin SA method.

Figure 1 shows the difference in UV-vis absorbance of multilayer films with alternating PAH and PSS layers prepared by spin SA and dip SA methods. The aqueous polyelectrolyte concentrations of PAH and PSS used in the two different deposition methods were all identical at 10 mM. At each deposition step, the spin SA process was performed at a spinning speed of 4000 rpm and there were two washing steps with pure deionized water at the same spinning speed. The dipping process was performed for an adsorption time of 20 min per layer, to allow enough time for saturated adsorption. The absorbance at 225 nm in the UV region was assigned to be the contribution from the adsorbed PSS chains. It should be noted at this point that the multilayer film fabricated by the spin SA method is adsorbed onto only one side of a quartz wafer, while the film prepared by the dip SA method is adsorbed onto both sides of a quartz wafer. The film thickness per bilayer adsorbed by the spinning process and the dipping process was found to be about 24 and 4 Å, respectively, as determined from ellipsometry measurements, when the same molar concentrations of the polyelectrolytes were used.

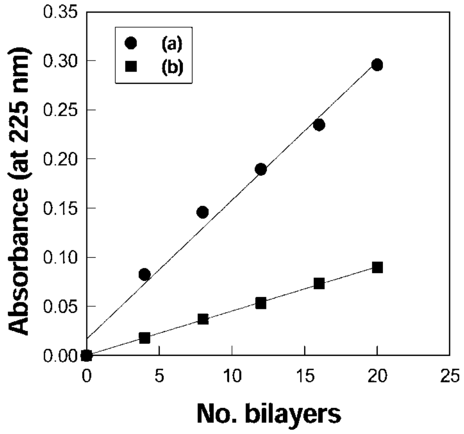

Fig. 1. Absorbance at 225 nm of PAH/PSS multilayers prepared by: a) spin SA method; b) dip SA method.

This significant difference in the adsorbed amount between the dipping and the spinning method is caused by different adsorption mechanisms. In the case of the conventional dip SA method, polyelectrolyte chains are allowed to diffuse toward the substrate under the influence of the electrostatic interaction and then the adsorbed chains rearrange themselves on the surface. On the other hand, the adsorption and rearrangement of adsorbed chains on the surface, and the elimination of weakly bound polymer chains from the substrate, in the spin SA process are almost simultaneously achieved at a high spinning speed for a short time. Fast elimination of water in the spinning process significantly increases the molar concentration of the polyelectrolyte solution during the short deposition time[7] and this increase in the polyelectrolyte concentration yields thick layers, despite the thin film formation typically provided by the centrifugal force and air shear force.[8–10] It also increases the electrostatic attraction between oppositely charged polymers because the presence of

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water molecules in the assemblies generally screens the electrostatic attraction. In other words, when water molecules are adsorbed onto a substrate, the preadsorbed water molecules may block polyelectrolyte adsorption onto the surface, and thus the surface coverage with polyelectrolyte chains may be incomplete. However, if polymer adsorption and water drainage are almost simultaneously realized in a short time, as in the case of the spin SA process, there would be more room for polyelectrolytes to adsorb onto the substrate. Figure 2 schematically represents these driving forces caused by the spinning process.

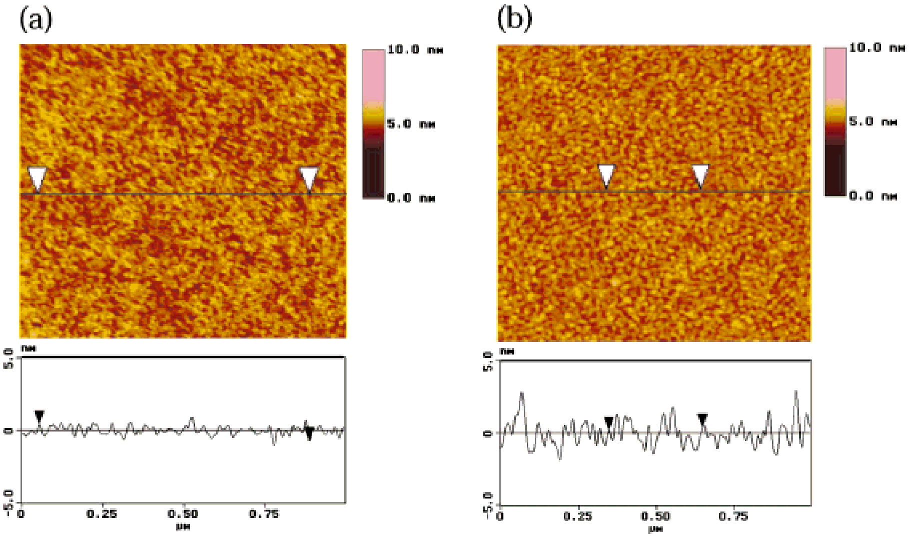

Fig. 3. a) Tapping mode AFM image (Digital Instruments, Nanoscope IIIa) of a $(PAH/PSS)_{30}$ film prepared with spin SA; b) $(PAH/PSS)_{30}$ film fabricated with dip SA.

We also found that the spin SA method has a significant effect on the surface roughness of prepared multilayer films, presumably because of the air shear force caused by the spinning process.[11] In order to investigate this effect in detail, we measured the surface roughness of the self-assembled films using atomic force microscopy (AFM). Figure 3a shows that the surface roughness of a spin SA film composed of $(PAH/PSS)_{30}$ bilayers was 3.1 Å. A $(PAH/PSS)_{30}$ film with 30 bilayers prepared by the dip SA method had a surface roughness of about 8.1 Å, despite the flattened adsorption of the polyelectrolyte onto the substrate due to the low ionic strength,[12] as shown in Figure 3b. These results are quite reproducible and demonstrate clearly that the air shear force driven by the spinning process significantly enhances the surface planarization of the multilayer films. In addition, the surface roughness of about 3.1 Å and the bilayer thickness of 24 Å for the spinning process, compared with 8.1 and 4 Å for the equivalent properties for the dipping process, provides indirect evidence that the internal structure of the spin SA films is highly ordered. This also points to the fact that the film prepared with the spin process contains rather distinct interfaces between respective layers in contrast to the film obtained by the dipping method, although the Bragg peaks in the X-ray reflectivity spectra of the PAH/PSS multilayer films cannot distinguish such internal structure due to the small electron density difference between PAH and PSS.

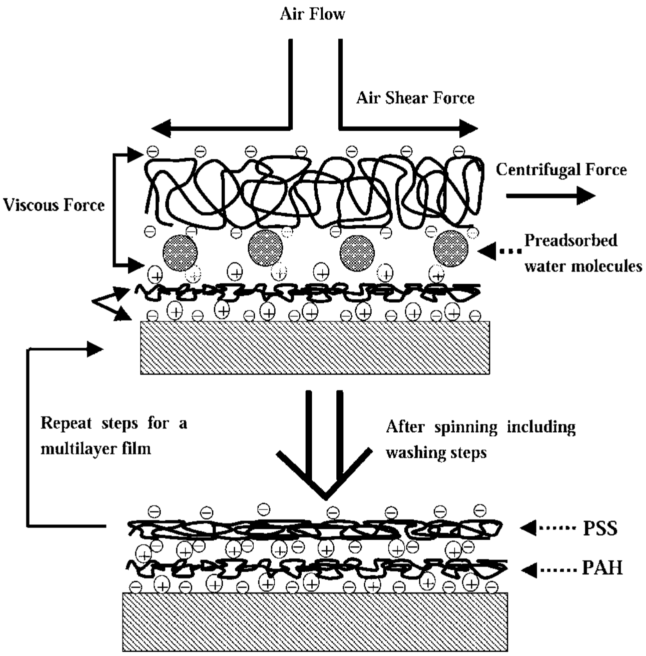

Fig. 2. A side view schematic depicting the build-up of multilayer assemblies by consecutive spinning process of anionic and cationic polyelectrolytes.

To confirm the hypothesis described above, we prepared negatively charged CdS nanoparticles with a diameter of about 2 nm and then investigated the internal structure of $[(PAH/PSS)_n/(PAH/CdS)_1]_m$ ($[n + 1] \times m = 20$ or 21) multilayer films, exploiting the significant electron density difference between a polyelectrolyte layer and an inorganic nanoparticle layer. As shown in Figure 4, all the multilayer films, with different numbers of the (PAH/PSS) bilayer in each repeat organic/inorganic layer ranging from 0 to 4, clearly exhibit Bragg reflection peaks originating from the internal structure. The surface roughness of the five different multilayer films measured from AFM is about 5 Å. It is particularly striking to note that the existence of Bragg peaks even in the $(PAH/CdS)_{20}$ film (composed of alternating a nanoparticle layer of 20 Å in diameter and a PAH layer of 6 Å in thickness) strongly indicates that each layer in the multilayer films forms an almost perfect superlattice layer carrying a sharp internal interface in spite of the ultrathin film of the organic layer.

However, in the case of a $(PAH/CdS)_{20}$ multilayer film prepared by the conventional SA method, the average bilayer thickness is about 6 Å and this bilayer thickness is much smaller than the average CdS nanoparticle size of 20 Å. In

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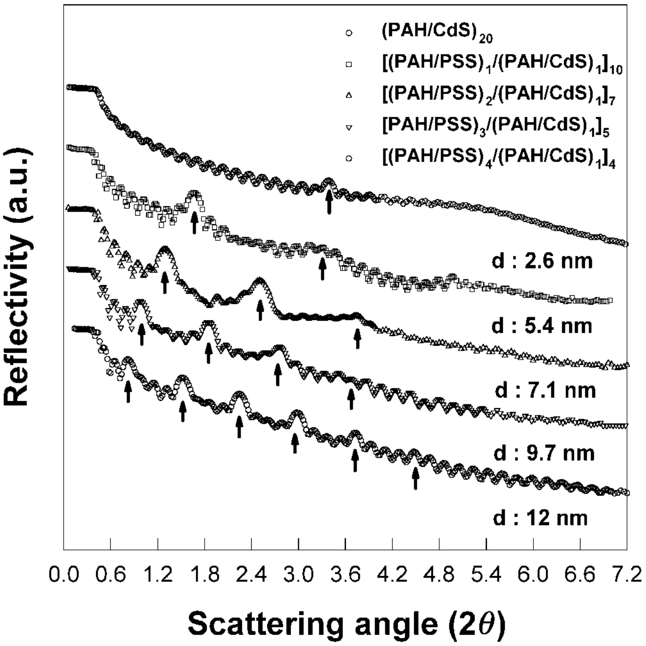

Fig. 4. X-ray reflectivity curves of [(PAH/PSS)$_n$/(PAH/CdS)$_1$]$_m$ ([n + 1] × m = 20 or 21) films prepared by the spin SA method. The increase of bilayer number of (PAH/PSS) from 0 to 4 causes the increase of d-spacing between polyelectrolyte and nanoparticle from 2.6 to 12 nm. The arrow symbols in the figure indicate the Bragg peaks of such an internal structure.

addition, the surface roughness of the film is found to be around 18 Å. This disagreement between the bilayer thickness and the nanoparticle size for a film prepared by the dipping method is believed to be caused by the insufficient surface coverage of respective layers and this further causes less electron density difference between organic and inorganic layer, as mentioned in several papers.[13–15] This distinct difference in the dip and the spin SA multilayer structures, shown schematically in Figure 5, indicates clearly that the spin SA method can easily provide the well-ordered internal structure, which cannot be achieved with the dip SA even containing a high ionic strength of the polyelectrolyte solution or multiple organic layers between inorganic particle layers.

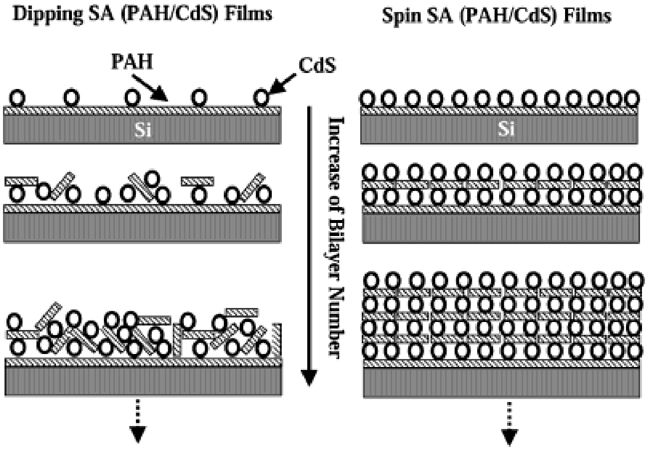

Fig. 5. Schematic diagram of the internal structure of (PAH/CdS)$_n$ films prepared by dip and spin SA methods.

In summary, we have demonstrated for the first time that the spin SA process utilizing centrifugal force, viscous force, air shear, and electrostatic interactions causes adsorption, the rearrangement of polymer chains onto a substrate, and the desorption of weakly bound chains in a very short time of approximately 10 s. This new ultrathin film-forming process, despite being much simpler and faster than the conventional dip SA process, yields a highly ordered internal structure far superior to the structure obtained with the dip SA process. It also allows us to predict and control precisely the bilayer thickness as well as the surface roughness.

Multilayer films based on hydrogen bonding and chemical bonding as well as the electrostatic attraction can also be fabricated by the spin SA method and these results will be presented in a forthcoming paper. In the light of wide application spectra of the ultrathin multilayer films, we strongly believe that the spin SA process developed in the present study will open up new possibilities for highly efficient electronic/photonic devices based on multilayer structures.

Experimental

PSS (Aldrich, M_w = 70 000) and PAH (Aldrich, M_n = 50 000–65 000) were used as anionic and cationic polymers, respectively. All the polyelectrolyte aqueous solutions were used without pH adjustment and the addition of ionic salt in this study. Anionic CdS nanoparticle solution of 6×10^{-4} M was prepared by treating Cd^{2+} ions with Na_2S in the presence of mercaptoacetic acid [16,17] and the nanoparticle size of CdS was measured to be about 20 Å, as confirmed by transmission electron microscopy (TEM) and AFM. We also found that the CdS nanoparticles were almost uniform in size.

Quartz substrates for the deposition of the polyelectrolytes were initially cleaned by ultrasonification in a hot mixture of H_2SO_4/H_2O_2 (7:3) for 3 h. They were then heated in a mixture of $H_2O/H_2O_2/NH_3$ (5:1:1) at 80 °C for 1 h, and then subsequently dried by N_2 gas purging. After this procedure, the substrates are negatively charged and used for the polyelectrolyte deposition starting with the cationic PAH. The deposition steps were carried out as follows: a few drops of polyelectrolyte solution were placed on the substrate and then the substrate was rotated with a spinner at a fixed rotation speed (typically, 4000 rpm) for 8–15 s. After the deposition of each polyelectrolyte layer, the substrates were thoroughly rinsed twice with plenty of deionized water. The spinning time and the speed for the washing step were identical to those for the layer deposition.

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[1] P. K. H. Ho, J.-S. Kim, J. H. Burroughes, H. Becker, S. F. Y. Li, T. M. Brown, F. Cacialli, R. H. Friend. *Nature* **2000**, *404*, 481.
[2] X. Zhang, J. Shen, *Adv. Mater.* **1999**, *11*, 1139.
[3] J. D. Mendelson, C. J. Barrett, V. V. Chan, A. J. Pal, A. M. Mayes, M. F. Rubner, *Langmuir* **2000**, *16*, 5017.
[4] A. Laschewsky, E. Wischerhoff, M. Kauranen, A. Persoons, *Macromolecules* **1997**, *30*, 8304.
[5] Y. He, S. Gong, R. Hattori, J. Kanicki, *Appl. Phys. Lett.* **1999**, *74*, 2265.
[6] G. Decher, J.-D. Hong, J. Schmitt, *Thin Solid Films* **1992**, *210*, 831.
[7] D. E. Bornside, *J. Electrochem. Soc.* **1990**, *137*, 2589.
[8] S. Middleman, *J. Appl. Phys.* **1987**, *62*, 2530.
[9] T. J. Rehg, B. G. Higgins, *Phys. Fluids* **1988**, *31*, 1360.
[10] F. Ma, J. H. Hwang, *J. Appl. Phys.* **1990**, *68*, 1265.
[11] F. C. Chou, P.-Y. Wu, *J. Electrochem. Soc.* **2000**, *147*, 699.
[12] Y. Lvov, G. Decher, H. Mohwald, *Langmuir* **1993**, *9*, 481.
[13] J. Schmitt, G. Decher, W. J. Dressick, S. L. Brandow, R. E. Geer, R. Shashidhar, J. M. Calvert, *Adv. Mater.* **1997**, *9*, 61.
[14] H. Hong, R. Steitz, S. Kirstein, D. Davidov, *Adv. Mater.* **1998**, *10*, 1104.
[15] M. Gao, B. Richter, S. Kirstein, H. Mohwald, *J. Phys. Chem. B* **1998**, *102*, 4096.
[16] M. Gao, X. Zhang, B. Yang, F. Li, J. C. Shen, *Thin Solid Films* **1996**, *242*, 284.
[17] L. Spanhel, M. Haase, H. Weller, A. Henglein, *J. Am. Chem. Soc.* **1987**, *109*, 5649.

0935-9648/01/1407-1078 $ 17.50+.50/0