# High-speed multilayer film assembly by alternate adsorption of silica nanoparticles and linear polycation

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**QCM showed that $SiO_2$/poly(diallyldimethylammonium chloride) (PDDA) film assembly could be achieved in 2 s for 45 nm silica nanoparticle monolayers and 20 s for PDDA monolayers, with film integrity demonstrated by SEM and spectroscopic ellipsometry.**

Layer-by-layer assembly of films containing nanoparticles and oppositely charged polyions provides a viable approach to advanced materials or devices with molecularly engineered properties.[1] Building on pioneering work of Iler,[2] who used oppositely charged colloidal particles to make films, linear polyions[3–6] have permitted materials such as dendrimers,[7] proteins,[8] latex[9] and inorganic nanoparticles to be incorporated.[10–14] For most materials used in layer-by-layer electrostatic film assembly, 6–15 min are required for every step of monolayer formation.[2–14] Here we show that time to assemble nanoparticle/linear polyion films can be decreased 100-fold.

Films were assembled with colloidal 45 nm diameter $SiO_2$ and linear quaternary ammonium polymer poly(diallyldimethyl-ammonium chloride) (PDDA, MW = 70 000) in 0.01 M NaCl at pH 9.5. Silica is negatively charged and PDDA is positively charged at this pH.[14] We monitored assembly with a quartz crystal microbalance (QCM, USI System, Japan)[14,15] in two modes. For stepwise measurement, a Ag- or Au-coated resonator was immersed alternately in polycation or silica solutions for a given period, dried, and the QCM frequency change measured. For *in situ* monitoring, only one side of the resonator was in permanent contact with the surface of the solution and the frequency change was recorded continuously. Films were assembled on electrodes of the QCM resonator by repeating alternate adsorption of PDDA and silica. From the Sauerbrey equation, taking into account characteristics of the quartz resonators ($F_o$ = 9 MHz), the following relation holds between adsorbed dry mass $\Delta M$ (ng) on the electrode of area $S$ = 0.16 cm$^2$ and frequency shift $\Delta F$ (Hz):[8,15]

$$-\Delta F = -1.83 \times 10^8\ \Delta M/S$$

For scanning electron microscopy (SEM, Hitachi S-900), a resonator with an assembled film was cross-sectioned and coated with a 20 Å Pt film. Film thicknesses were measured from cross-sectional images.[14]

Spectroscopic ellipsometry[16] at incidence angles of 70, 72, 76 and 78° and wavelengths of 300–1000 nm was done on films deposited on silicon (100) with native oxide to determine thickness and optical constants using a variable angle spectroscopic ellipsometer (Woollman Co.)

Fig. 1 shows *in situ* QCM of alternate PDDA and $SiO_2$ adsorption without intermediate sample drying. In the first step, PDDA was adsorbed onto a Ag electrode. QCM frequency decreased during the first 60 s, after which a slower change was observed as adsorption saturation set in. Then, the resonator was immersed in pure water (black dots) for washing. Next, the film was immersed in a $SiO_2$ dispersion and silica adsorption saturation occurred in several seconds. After subsequent water washing, the film was immersed again in PDDA solution, and so on. Each step was reproducible and the adsorption process reached 90% saturation in 10 s for $SiO_2$ and 40 s for PDDA.

To find the minimum time for producing good quality films, we tested adsorption times from 15 min to 2 s, drying the films after every other deposition step. Linear growth of film mass and thickness with adsorption cycle number was observed in most cases. The QCM frequency shift was $-\Delta F$ = 1200 ± 60 Hz for $SiO_2$ and 100 ± 10 Hz for PDDA for 15 min adsorption. A minimal time for the process was found for assembled multilayers by decreasing time and monitoring $\Delta F$ corresponding to each layer. For 15 min, 10 min, 5 min, 1 min and 20 s PDDA adsorption gave $-\Delta F$ = 100 Hz. For $SiO_2$ minimal adsorption time was 2 s, with $-\Delta F$ = 1200 Hz. $SiO_2$/PDDA assembly with less than 2 s/20 s adsorption times deteriorated the film growth process. Sample drying after every PDDA deposition was necessary for regular multilayer growth.

We also analyzed the structures of $(SiO_2/PDDA)_{6-24}$ films assembled with 2 s/20 s adsorption times with drying after every deposition step (Table 1). Fig. 2 gives a typical SEM image of such a $SiO_2$/PDDA film. The image shows densely packed silica spheres and its surface is smooth on the level of one silica sphere (*ca.* ±40 nm). $SiO_2$/PDDA bilayer thickness was estimated from total film thickness and number of adsorption cycles. For six films assembled with 2 s/20 s times $\langle d \rangle$ = 24.6 ± 0.4 nm, the same as for $SiO_2$/PDDA assembled with 'traditional' 15 min adsorption steps. This corresponds to mean thickness of closely packed spheres of 45 nm diameter and indicates complete surface filling.

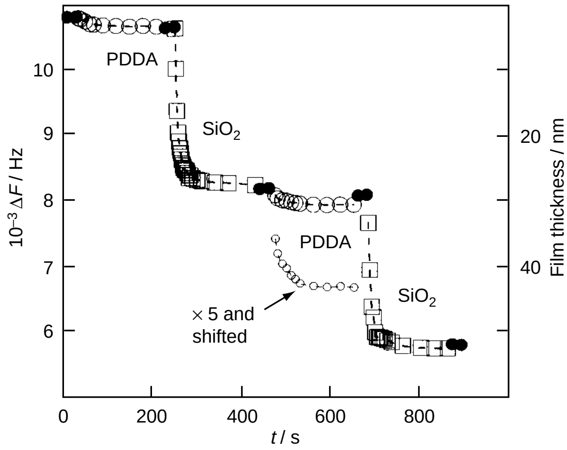

**Fig. 1** QCM monitoring of PDDA and $SiO_2$ sequential adsorption on a silver electrode: PDDA (○), intermediate water-washing (●) and $SiO_2$ (□). The third step PDDA curve drawn with 5× amplification. 45 nm diameter $SiO_2$ was used at 10 mg ml$^{-1}$ (Nissan Kagaku, Japan) and 3 mg ml$^{-1}$ linear poly(diallyldimethylammonium chloride) (PDDA, MW = 70 000, Aldrich) were used in 0.01 M NaCl at pH 9.5.

**Table 1** Structural parameters of 45 nm $SiO_2$/PDDA films assembled with 2 s/20 s adsorption

| No. of bilayers/ substrate | Total QCM $\Delta F$/Hz | Mass from QCM/ $10^6$ g $cm^{-2}$ | Thickness/nm (SEM) | Thickness/nm Ellipsometry | Film density/ g $cm^{-3}$ |
|---|---|---|---|---|---|
| 4/Si | | | | 99 | |
| 6/Si | | | | 149 | |
| 7/Si or Ag | 8400 | 23.0 | | 173 | 1.38 |
| 8/Au | 11200 | 30.6 | 210 | | 1.45 |
| 20/Ag | 24500 | 67.0 | 480 | | 1.40 |
| 24/Ag | 33000 | 90.2 | 610 | | 1.48 |

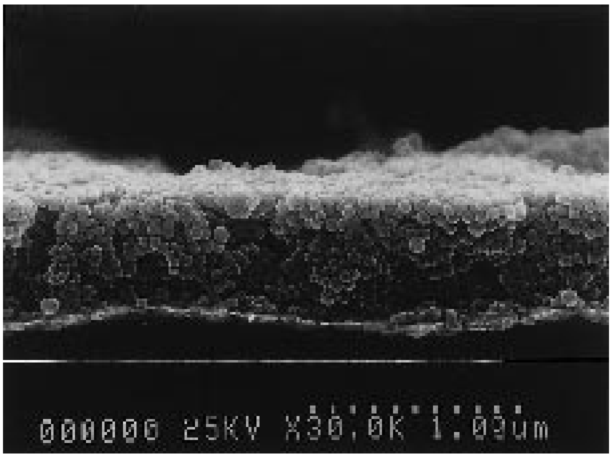

**Fig. 2** SEM cross-sectional view of {PDDA+ (45 nm $SiO_2$/PDDA)$_{24}$} film deposited using the 2 s/20 s monolayer adsorption on silver electrode

Ellipsometric data were modeled with a Lorentz oscillator for an effective medium approximation,[16] to take into account the film's surface inhomogeneities and voids (*cf.* Fig. 2). A graph of $\psi$ and $\theta$ values of the seven-bilayer film is given in Fig. 3. The film refractive index at 633 nm was estimated at 1.25, *i.e.* $< 1.48$ for pure silica.

Bilayer thicknesses from QCM, SEM and ellipsometry for films assembled on different substrates agree very well (Table 1). Average density of $SiO_2$/PDDA multilayers is $<\rho> = 1.43 \pm 0.05$ g $cm^{-3}$. To calculate the silica packing coefficient in the films, we assumed that the dry film consists of $SiO_2$, PDDA and air-filled pores. The mass ratio for PDDA to PDDA/$SiO_2$ is 100 Hz/1300 Hz = 0.077. Taking into account component densities[14] ($<\rho> = 1.43$, $\rho_{SiO_2} = 2.2$ and $\rho_{PDDA} = 1.1$ g $cm^{-3}$) we obtain the volume ratio $V_{PDDA}/V_{bilayer} = 0.1$. From the equation $\rho_{PDDA}\ V_{PDDA} + \rho_{SiO_2}\ V_{SiO_2} + \rho_{air}\ V_{air} = <\rho>\ V$, where the air-term is very small, $V_{SiO_2}/V = 0.6$. This is very close to the theoretical dense-packing coefficient for spheres (0.63), and corresponds to details in the SEM micrographs. $SiO_2$/PDDA film volume composition is: 60% $SiO_2$ + 10% polycation + 30% air-filled pores. These pores are formed by closely packed 45 nm $SiO_2$ and have a typical dimension of 20 nm. The films have controlled pores which could be varied by the choice of nanoparticle diameter.

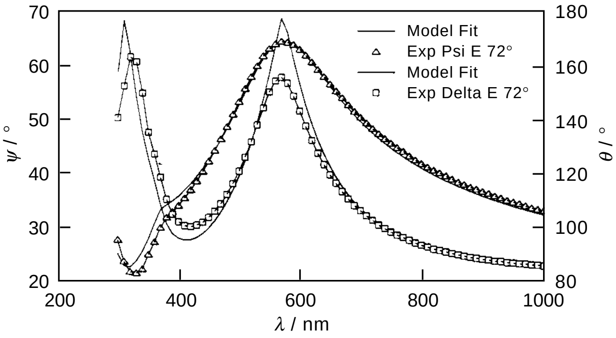

**Fig. 3** Ellipsometric measurements of {PDDA + (45 nm $SiO_2$/PDDA)$_7$} film thickness on silicon wafer: $\psi$ and $\theta$ values of the film at 72° incidence and the model fit (see text). Lorentz oscillator constants were determined simultaneously with thicknesses (Table 1) as Am 1.2 = 240 ± 6, Br1.2 = 1.9 ± 0.2, En1.2 = 20.5 ± 0.3.

We estimate the diffusion limitation for surface coverage $A(t)$ by adsorption from solution of particles with diffusion coefficient $D$[4,17] from $A(t) = 2/\pi C(Dt)^{1/2}$. For $t = 2$ s, $C = 10$ mg $cm^{-3}$ and assuming for 45 nm silica $D = 1.1 \times 10^{-7}$ $cm^2$ $s^{-1}$,[18] $A \approx 3 \times 10^{-6}$ g $cm^{-2}$ and the layer thickness $L = A(t)/<\rho> \approx 21$ nm. This is reasonably close to the experimental silica layer thickness of 24.6 nm. Thus, 2 s corresponds roughly to the diffusion limited time for $SiO_2$ monolayer adsorption.

Similar estimates for diffusion limits on PDDA show that in 20 s a hundred monolayers could be delivered to the surface. 20 s does not correspond to diffusion limited adsorption. Hence, conformational changes upon adsorption probably govern the time needed to make uniform monolayers. The mechanism of PDDA relaxation is not clear, but sample drying speeds the process. Relevant ideas about kinetics of polycation adsorption on a charged surface have been discussed.[19]

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## Notes and References

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