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Communications

Self-Assembled Cobalt–Diisocyanobenzene Multilayer Thin Films

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Self-assembled multilayers are of interest for a variety of applications because of the potential for controlling individual layer composition and properties within layered assemblies on surfaces. Such potential applications include use as active components in nonlinear optical devices,^{1,2} stable charge-separated assemblies,³ and materials with selective chemical responses for sensor applications.^{4,5} Among the different chemical strategies which have been developed to date for multilayer self-assembly,^{1,4,6–9} multilayers prepared by alternate deposition of metal ions and bis(phosphonate) moieties onto an appropriately functionalized sub-

strate^{10,11} are currently under intense investigation for all of these applications.^{2,3,5} The metal–bis(phosphonate) (MBP) system provides well-ordered multilayer films made of alternating organic and inorganic layers that are robust and relatively easy to prepare.

To increase the number of potential applications and to expand the types of chemistry available for building multilayer structures, we have been developing alternative “inorganic/organic” systems suitable for self-assembly of multilayer films. In particular, we have developed systems based on transition-metal coordination chemistry¹² which provide new opportunities for preparing self-assembled multilayers and for building superstructures. Several other examples of multilayer deposition utilizing metal–ligand coordination chemistry have been reported recently including pyrazines with Ru,¹³ dithiols with Cu,¹⁴ diamines with Ru,¹⁵ and diamines with Ni–Pt(CN)₄.¹⁶ We report here a new self-assembly system based on a the cobalt–diisocyanide system. This system utilizes the strong coordination of the isocyanide ligand to a metal center as demonstrated by Feinstein-Jaffe et al.,¹⁷ who made two- and three-dimensional polymers consisting of rhodium(I) and several diisocyanides.

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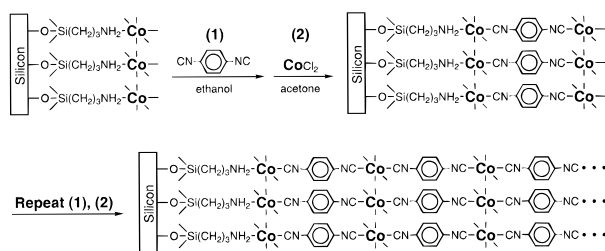


Figure 1. Synthesis of cobalt–diisocyanobenzene multilayer films.

Cobalt–1,4-diisocyanobenzene (Co–DiCNB) multilayer films can be prepared by starting with an amine-functionalized surface.¹⁸ We have previously determined¹² that when amine-terminated surfaces are exposed to a nonaqueous CoCl_2 solution, Co ions bind strongly and are not readily displaced, even by subsequent washing with ethanol or acetone. Coordination of another amine to the bound cobalt is inefficient; it is either extremely slow or attachment is extremely labile.¹² However, isocyanide ligands do bind strongly to the surface-bound cobalt ions, as evidenced by the data shown below for the Co–DiCNB system. Alternate dipping of an amine-functionalized silicon wafer in cobalt and diisocyanobenzene solutions results in the deposition of regular multilayers, as illustrated in Figure 1.¹⁹

The new cobalt–diisocyanide system shares an important feature with several other systems developed for multilayer self-assembly in that chemical “activation” or “deprotection” of monolayer surface functional groups is not necessary to build multilayers. This feature makes multilayer preparation straightforward and eliminates exposure of the film to harsh conditions often necessary to activate surface functional groups.

Film thicknesses of Co–DiCNB multilayers were characterized at regular intervals during growth using optical ellipsometry.²⁰ The results of ellipsometry measurements on three sets of samples are shown in Figure 2. Samples 1 and 2 were prepared using a 10 mM solution of CoCl_2 in ethanol, while samples 3–6 were prepared using acetone as the CoCl_2 solvent; each sample utilized ethanol solutions of 1,4-diisocyanobenzene. Film thickness is shown to increase linearly for each set. Samples 1 and 2 show linear layer growth to 50 layers (only 25 layers are shown) and the average layer thickness is determined to be 5.5 Å/layer. This is significantly less than the ~ 11.6 Å/layer expected for diisocyanobenzene molecules oriented normal to the surface.²¹ The small layer thicknesses suggest that the

(18) Silicon wafers are functionalized using 3-(aminopropyl)triethoxysilane via refluxing in a 1% (v/v) 3-(aminopropyl)triethoxysilane/ethanol (200 proof) solution overnight, rinsing with ethanol, and drying with flowing N_2 .

(19) Cobalt–diisocyanide multilayer samples 1 and 2 were prepared by submersing an amine-functionalized wafer alternately in a 10 mM solution of CoCl_2 in ethanol for 4 h (followed by rinsing with acetone) and in a 10 mM solution of diisocyanobenzene in ethanol overnight (followed by rinsing with ethanol). Samples 3–6 were prepared by submersion in CoCl_2 /acetone for 30 min followed by the DiCNB solution for 90 min. Experiments have shown that these soak times give optimal layer thicknesses as determined by ellipsometry.

(20) Ellipsometry was done using a Rudolph thin-film ellipsometer 43702-200E with a tungsten halogen light source and a 632 nm filter. Thicknesses were calculated using DafIBM (version 2.1) provided by Rudolph, assuming an index of refraction of $3.858 - 0.018i$ for the silicon substrates.

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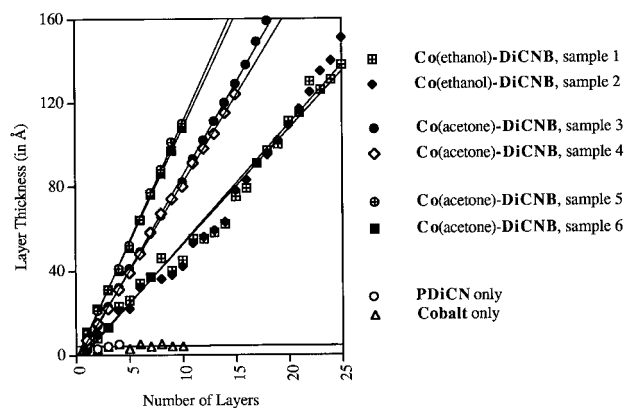


Figure 2. Layer thicknesses of Co–DiCNB multilayer thin films as measured by ellipsometry.

DiCNB molecules are oriented at an angle of $\sim 62^\circ$ from the surface normal if the surface coverage is complete. If adjacent cobalt–diisocyanobenzene moieties within a layer are closely packed, π -stacking interactions might be expected to orient the aryl groups normal to the surface. However, if the Co–DiCNB moieties are farther apart, the π -stacking interactions might actually force the DiCNB molecules to tilt from the normal in order to interact with adjacent molecules.

For the samples prepared with CoCl_2 /acetone solutions (samples 3–6), the average layer thickness was found to be ~ 8.5 Å/layer for samples 3 and 4 and ~ 11.2 Å/layer for samples 5 and 6, corresponding to diisocyanide molecules tilted $\sim 43^\circ$ and $\sim 0^\circ$ from the surface normal, respectively. The only difference in the preparations of these two sets of samples is that samples 3 and 4 were prepared with a different ethanolic DiCNB solution (same concentration) than that used for samples 5 and 6. We postulate that impurities or water content differences in the two DiCNB solutions may be responsible for the differences in average layer thicknesses between these two sets of samples. Work currently in progress addresses optimizing solvents, solution composition, and soak times for the current reagents as well as incorporating alternate organic moieties such as diisocyanohexane or 4,4'-biphenyl diisocyanide.

Interestingly, for a given sample the layer thicknesses are fairly uniform, but there can be variation from sample to sample as mentioned above. This phenomenon has also been observed for MBP multilayers,²² in which case surface functionalization and the associated density of surface binding sites appear to be critical in determining the thickness of subsequent individual layers. Once the binding site density is established in the first layer, it is perpetuated as layers are grown. This may also be a factor in the thickness variation of the Co–DiCNB multilayers reported here.

Ellipsometry data for two control samples are also shown in Figure 2. These samples were prepared by submersing amine-functionalized wafers in solutions of either cobalt in acetone or diisocyanide in ethanol, rinsing the wafer in the respective solvent, and repeating with the same reagent. This experiment was performed to demonstrate that layer growth does not occur with only one of the reagents.

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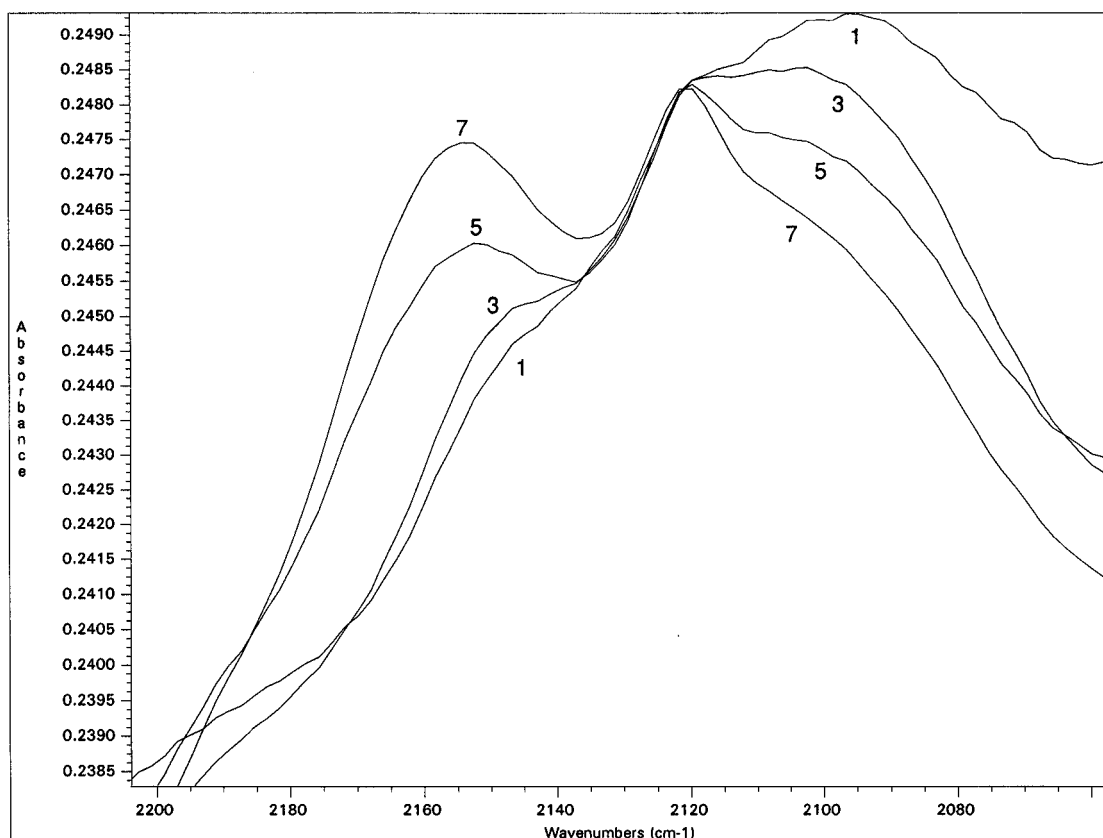


Figure 3. ATR-FTIR data of Co-DiCNB multilayers grown on a Si ATR crystal showing increasing isocyanide absorbance with 1, 3, 5, and 7 layers.

The estimated index of refraction used for calculating thicknesses from ellipsometry data was $1.50 + 0i$. This estimate was based on comparison of ellipsometry data to grazing angle X-ray diffraction data,²³ which gives a more accurate measurement of film thickness independent of the optical index of refraction of the film.^{22,24} Grazing angle diffraction was observed for multilayer films with more than ~ 10 layers, indicating reasonably uniform film thicknesses. Grazing angle X-ray diffraction data for sample 1 of Figure 2 with 27 layers indicates the layer thickness was ~ 148 Å, which compares well with ellipsometry results.

Attenuated total reflectance FTIR (ATR-FTIR) spectra²⁵ of the isocyanide stretch region for a Co-DiCNB sample prepared on an amine-functionalized silicon ATR crystal are shown in Figure 3. This region of the IR is highly specific for aryl isocyanides. These spectra show a strong absorbance at 2121 cm^{-1} assigned to an unbound aryl isocyanide stretch as well as a peak at 2155 cm^{-1} attributable to a metal-coordinated aryl isocyanide stretch. The ratio of the peak areas²⁶ associated with bound isocyanide to unbound isocyanide is plotted in Figure 4 and is shown to increase linearly. This is expected for the layering sequence in Figure 1 since all films studied were terminated with a DiCNB layer. As more layers are added, the amount of unbound R-NC groups should remain fairly constant,

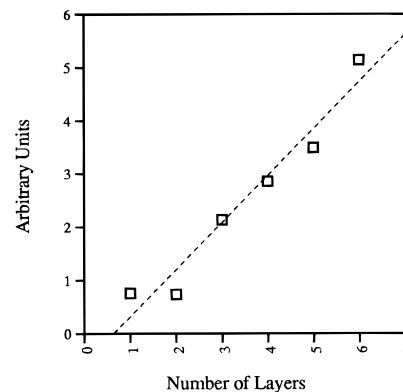


Figure 4. Ratio of the bound isocyanide peak area vs unbound isocyanide peak area.²⁶

while the number of bound R-NC groups should increase regularly. The best peak deconvolutions indicate the presence of four peaks: in addition to strong peaks at 2121 and 2155 cm^{-1} , a feature is observed at 2090 cm^{-1} corresponding to unbound isocyanide (most prominent in spectra of samples with few layers) and a small shoulder at 2185 cm^{-1} that is probably associated with an isocyanide bound to Co with either a different coordination environment or a different oxidation state.

XPS was performed on sample 1 to determine the approximate elemental composition of the 50-layer sample.²⁷ Preliminary results are qualitative and in-

(23) Grazing angle X-ray diffraction was measured using a Scintag XDS-2000 θ - θ powder diffractometer while scanning at low angles to observe interference between X-ray reflection from the front and back of the thin films.

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(25) ATR-FTIR spectra were obtained using polished $50 \times 10 \times 3$ spp 45° silicon parallelogram ATR crystals using a Harrick TMP-220 ATR attachment on a Nicolet Magna IR Model 550 FT-IR spectrometer.

(26) Peaks were deconvoluted and peak areas were determined using Spectracalc, version A2.23 (Galactic Industries).

(27) X-ray photoelectron spectroscopy (XPS) was done using a Perkin-Elmer 550 operated at 15 kV, 300 W to produce Mg K α X-rays at 1253.6 eV ; the average operating pressure was 1.4×10^{-8} Torr. Survey scans were done using a 45° takeoff angle.

dicating the presence of all of the elements expected. The C/N ratio was found to be 5.6:1. This is larger than the 4:1 ratio expected for 1,4-diisocyanobenzene, but the excess carbon could be attributed to solvent (ethanol or acetone) trapped in the film or to environmental sources of carbon. The C/Si ratio was found to be 47:1. This result indicates that the surface coverage is very good and little bare silicon was detected. The N/Co ratio was 18:1. Ideally this ratio should be close to 2:1 if the simple structure shown in Figure 1 reflects the actual structure; however, the film was terminated with a DiCNB moiety, and therefore more nitrogen would be present near the surface. Additional DiCNB molecules coordinated to Co either alone or as "lateral bridges" between adjacent Co centers could also be a source of the large N/Co ratio. Furthermore, XPS is known to be an extremely surface sensitive technique,²⁸ and we have not corrected for the photoelectron mean free paths.

An additional XPS experiment was performed to address the incorporation of solvent molecules and noncoordinated diisocyanide molecules. Sample 3 was heated overnight in a drying oven at 105 °C. The total layer thickness by ellipsometry was found to decrease by about 35%. Although this decrease could be due to sample decomposition or formation of a new material produced by annealing, it is more likely at these temperatures that the decrease is a result of solvent removal and some associated structural reorganization. In the related (hydrated) Rh-diisocyanide system, Feinstein-Jaffe et al. performed thermogravimetric analysis (TGA) indicating that water was released in the temperature range 100–200 °C and thermal decomposition did not occur below ~400 °C.¹⁷ Thus it is unlikely that decomposition is the source of film shrinkage. XPS of this "dried" film showed a significant decrease in carbon and oxygen signals and a marked increase in cobalt signal. The resulting N/Co ratio was 4.5:1, which is much closer to the "predicted" 2:1 value.

A larger Co signal (and consequently a better signal-to-noise ratio) makes this method for analyzing the films appear to be more reliable. Further studies to validate and systematically monitor the "drying" process and to quantitatively determine the composition of the films via XPS are underway.

In summary, we have developed a novel cobalt-diisocyanobenzene system for self-assembly of multilayer thin films on an amine-functionalized silicon surface. The results presented here indicate that this system gives uniform layers which contain both Co and DiCNB components. Thickness measurements suggest that the DiCNB moieties are oriented from essentially 0° to ~40° from the surface normal for samples prepared using CoCl₂ in acetone. Studies continue to optimize the layer thickness, order, and reproducibility of the system, as well as to determine the structure and the exact composition of these films. This system not only provides an alternative to MBP chemistry for assembling multilayers without chemical activation of surface groups but also provides an additional "inorganic/organic" system which can be *combined with* MBP chemistry to grow "hybrid" superstructures with alternating metal-bisphosphonate and cobalt-isocyanide layers; this is a current goal of our research.

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