

Electrostatic Self-Assembly Processing of Materials and Devices

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ABSTRACT

Electrostatic self-assembly (ESA) methods have been used to synthesize multilayered thin film organic/inorganic materials and devices. The ESA method involves the dip coating of charged substrates with alternating layers of anionic and cationic molecules, and the properties of the resulting multilayered structures depend on both the characteristics of the individual molecules and the spatial order of the layers. Since the process is performed at room temperature and pressure by dipping substrates into separate solutions containing the charged molecules, coatings may be formed on substrates of virtually any composition, shape and size. Materials that have been investigated for incorporation into such coatings include noble metal nanoclusters, metal oxide nanoclusters, polymers, cage-structured molecules such as fullerenes, proteins, and dipolar chromophore molecules. Such materials have potential applications in photonic and electronic devices.

Keywords: electrostatic self-assembly, electro-optics, thin film, organic/inorganic composite, optical modulator

1.0 INTRODUCTION

Conventional photonic and electronic devices are fabricated using lithographic patterning and etching methods that have been developed during the past thirty years. Practical limitations of such "top-down" materials processing are posed by methods to precisely focus lithographic radiation, the spatial resolution to which multiple layers may be registered during the multi-step fabrication process, and the materials properties of both substrates and resists.

An alternative approach to such conventional lithography is the "bottoms-up" processing of materials and devices starting instead at the molecular level. This paper discusses one of the approaches to the formation of precisely dimensioned multi-layer thin films and thin film devices by this approach. So-called electrostatic self-assembly (ESA) or layer-by-layer (LBL) processing allows the formation of thin and thin films from many individual monolayers in which each of the monolayers is formed from molecular constituents that are selected in advance based on their specific engineering properties [1-6].

2. ELECTROSTATIC SELF-ASSEMBLY PROCESSING

This section reviews the basic model of how the ESA process allows the formation of thin films that may be used to form single layer and nanostructured multilayer materials and devices. First, the formation of alternating monolayers of simple polyelectrolytes is shown schematically in Figure 1. On the left, the substrate surface has been thoroughly cleaned and functionalized so the outermost surface layer effectively has a net negative charge. It is assumed that this net surface-charged substrate is dipped into a solution containing water soluble "cation" polymer molecules that have net positively charged functional groups fixed to the polymer backbone.

Because the polymer chain is relatively flexible, it is free to orient its geometry with respect to the substrate in response to electrostatic forces between the charges on the substrate and the charges associated with functional groups along the polymer chain. The functional groups move on the molecular level so a relatively low energy configuration is achieved in the

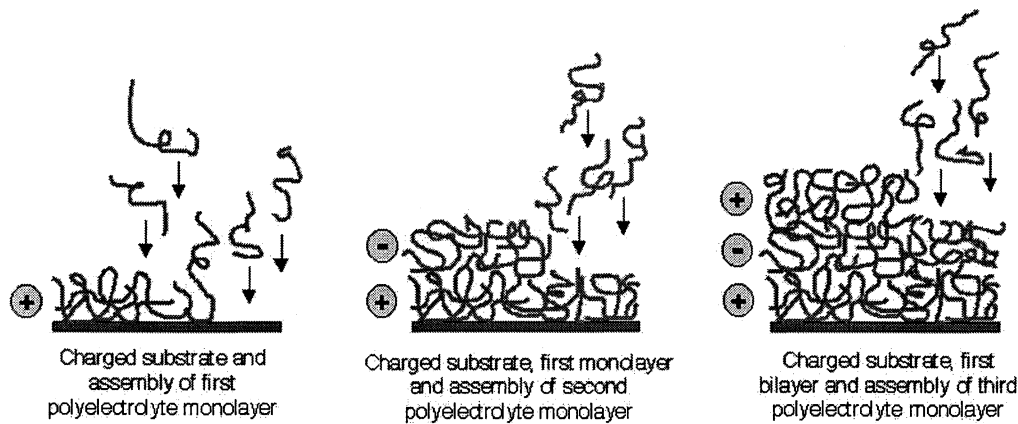


Figure 1. ESA Process Model for Formation of Multilayered Polymer/Polymer Thin Film Materials.

neighborhood of each group. For example, according to this very simple model for the deposition of the first monolayer, some of the positively charged functional groups along the cationic polymer chain experience attractive ionic forces toward the negatively charged substrate, and the polymer chain is bent as shown in response to those forces.

At the molecular level, the net negative charge at the surface of the substrate is thus masked from the electrostatic forces due to other positive groups located along the polymer chain. Those positive groups thus feel net electrostatic forces due to the fixed positive functional groups bonded to the substrate surface, and move away from that surface to form a net positive charge distribution on the outermost surface of the coated substrate. Since the net charge on the total polymer layer is neutral, negative charges with relatively loose binding to the polymer network pair up with these positive ions. Subsequent polyanion and polycation monolayers are added layer-by-layer, to produce the multi-layer structure as shown. The physical properties of the single layer and multilayer thin-films fabricated using this method are determined by both the properties of molecules that form the individual monolayers, and the physical ordering of the multiple monolayers through the thickness of the formed thin film.

Figure 2 shows the results of similar ESA processing where appropriately charged inorganic nanocluster quantum dots are substituted for the polymer layers. Note that for simplicity in the cartoon in Figure 2, the relative sizes of the clusters and the polymer layers are not to scale. Typically, nanoclusters on the order of 5 nm or less in cross-sectional dimension are separated by polymer interlayer spacers that well less than 1 nm in thickness. Further, the polymer interlayer spacer is nonplanar, and the particle layers interpenetrate to form a uniform particle distribution at the molecular level. Note also that through proper processing, both polymer layers may be substituted with nanocluster layers to affect significant changes in the properties of the resulting thin films.

The formation of stable colloidal solutions of the clusters is an important part of this process. Surface passivation using ultrathin polymer or other coatings allows stability of the clusters during storage prior to processing, as well as the avoidance of multi-particle agglomeration and resulting potential nonuniformities in the structure and properties of the resulting multilayered thin film.

The third part of the ESA model that may be used for the fabrication of multilayer functional materials involves the ability to vary the properties of the material through its thickness. Figures 1 and 2 show simple ABABAB structures, where A represents one of two molecular species and B the other. Figure 3 shows alternative structures that, by the incorporation of other layers, say C, D, E and F, and the variation of the order of multiple molecules, allow the formation of (1) multi-segment

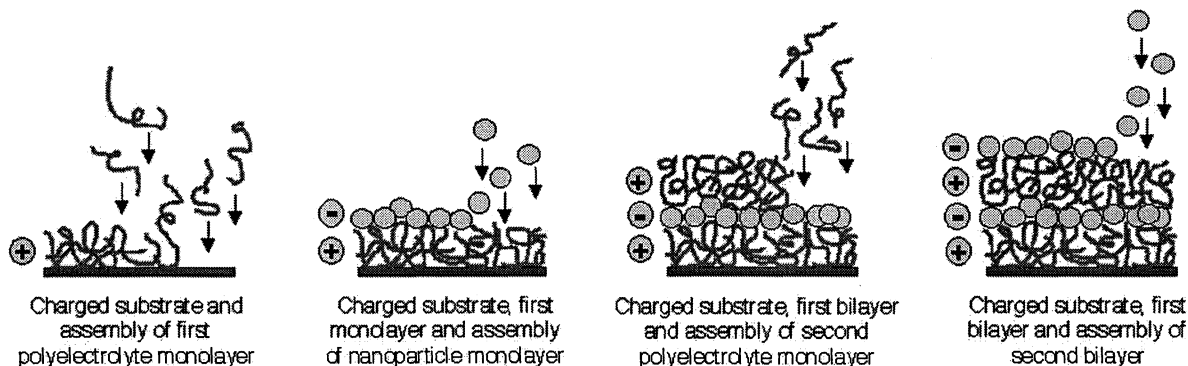


Figure 2. ESA Processing of Multilayered Nanocluster/Polymer Thin Film.

materials in which each several-monolayer segment is composed of a different pair of initial monolayer materials having a different property, (2) multisegment materials in which each segment has a property obtained by combining two or more individual molecules with different properties, or (3) segments or multiple segments in which properties are graded through the thickness by gradual variation of properties at the monolayer level. Examples of where such rules for the formation of mixed media systems may be of use are (1) waveguides, (2) Rule of Mixtures formation of materials having properties different from those obtainable using single materials alone, and (3) graded index of refraction or coefficient of thermal expansion.

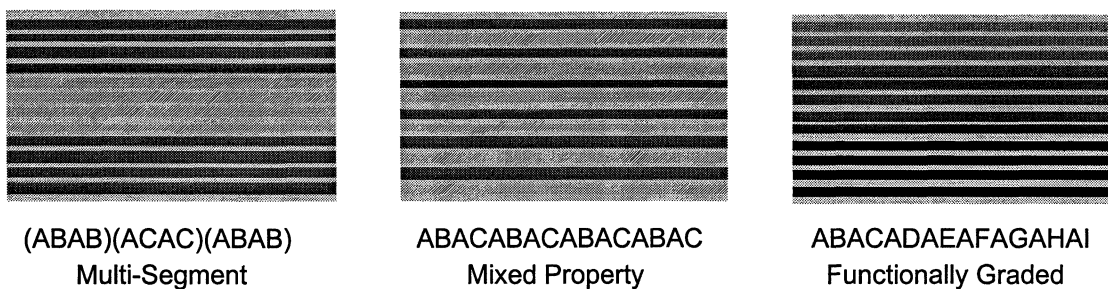


Figure 3. Layer-by-Layer ESA Processing May Be Configured to Yield Segmented (left), Mixed (center) and Graded-Property (right) Coatings.

Of additional interest is what occurs if the molecules used in each of the monolayers, or in every other monolayer, are dipolar in nature. It is found that the dipoles in those layers inherently self-align due to the electrostatic forces that control their adsorption from solution and ionic bonding to the last substrate surface. Such self-alignment is potentially an attractive alternative to the electric field poling of polymer-based electro-optic materials that contain dipolar molecules.

3. SUMMARY OF REPRESENTATIVE ESA FORMED MATERIALS PROPERTIES

ESA processes have been used to form thin film materials having a variety of potentially useful engineering functionalities. The design of such materials begins with an estimation of required functionality and a selection of appropriate molecules for each layer. The molecules are made water-soluble, then dissolved in water solutions to allow the multi-step dip processing described above. During the ESA process itself, characterization may be performed to verify the stability of thin film material

growth, according to the ESA models shown in Figures 1 and 2. Such measurements may include (1) water contact angle measurements, used to verify that the isoelectric point of the outermost layer of the film varies between alternating high and low values that are associated with the cationic and anionic monolayer materials, (2) ellipsometry, used to quantify the linear increase in total deposited ESA film thickness with the number of cationic/anionic bilayers deposited, (3) UV-vis spectroscopy, also used to verify film thickness increase, through measurement of optical attenuation through the film due to material adsorption, and potentially other analysis methods.

Figure 4 shows data typical of that associated with multilayer thin film fabrication. Shown is data indicating (a) alternating water contact angle at the outermost surface of a Al_2O_3 cluster/polymer multilayer film, which confirms alternating deposition of different molecular species with addition of consecutive monolayers, as in Figure 2 [7], (b) UV-vis absorption data for Fe_3O_4 cluster giant magnetoresistance (GMR) films, showing that molecular adsorption during processing is linear with the number of bilayers deposited [8], (c) ellipsometry data for PPV-based light emitting diode (LED) precursors, again confirming linear increase in thickness with addition of bilayers [9], and (d) Auger data of a multicomponent $\text{Al}_2\text{O}_3/\text{ZrO}_2/\text{Pt}$ film on a silicon substrate, illustrating graded property control versus depth through the material [3].

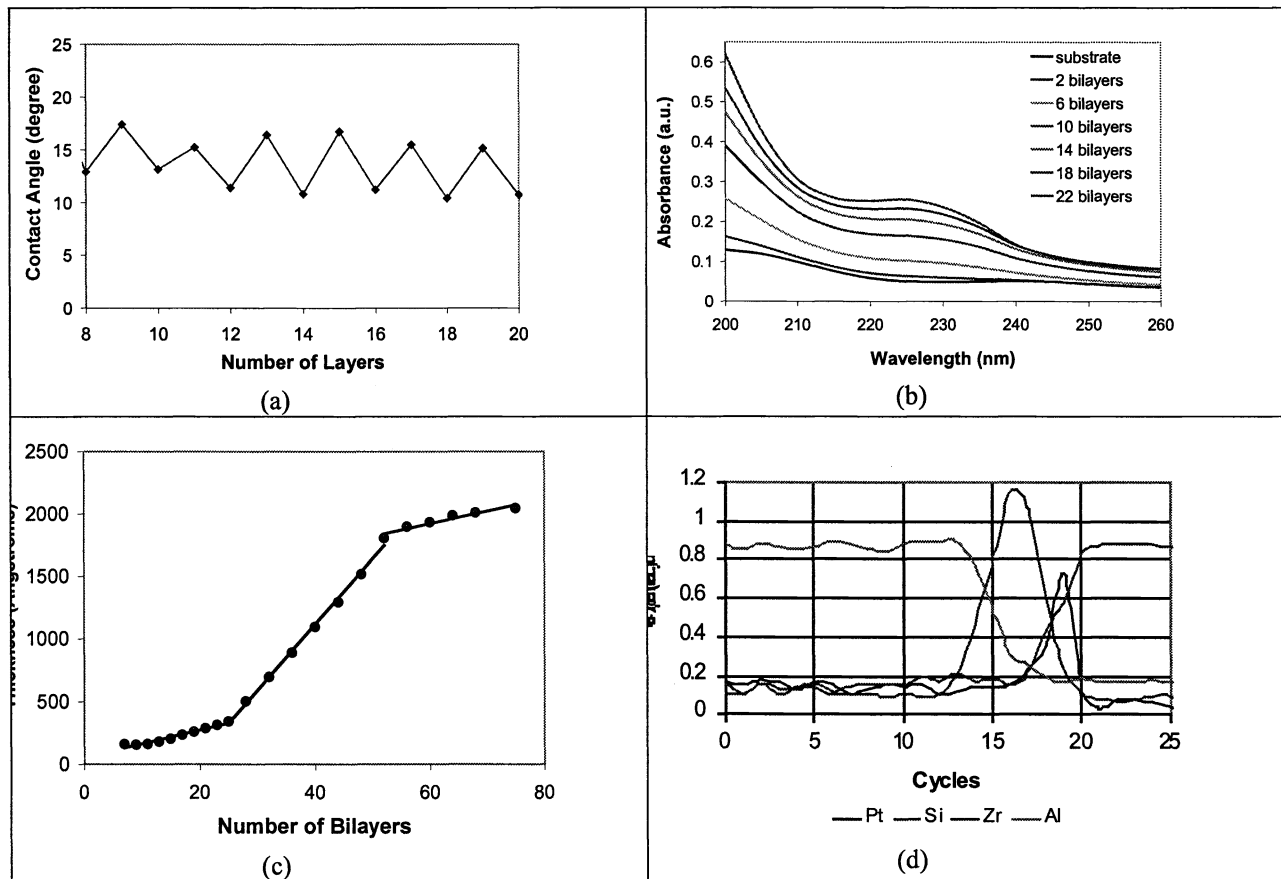


Figure 4. Typical Experimental Data for ESA Synthesis of Representative Coatings. Contact Angle (top left) Allows Analysis of ESA Process, UV-vis Absorption (bottom left) and Ellipsometry (top right) Indicate Film Growth Mechanics; Auger Scan of Al_2O_3 - ZrO_2 - Pt Cluster Film on a Single Crystal Si Substrate (lower right) Indicates Functionally-Graded Structure.

Representative material properties that have been demonstrated for ESA-formed thin films include electrical conductivity on the order of that of bulk metals for noble metal nanocluster-based thin films as thin as several tens of nanometers [10], electro-optic r_{33} coefficients greater than 40 pm/V [11], piezoelectric d_{33} coefficients greater than 100 pC/N. Combinations of thin film layers having different properties may allow the formation, for example, of electrode-active material-electrode sandwich devices [12].

4. DISCUSSION

ESA processing is a simple and exciting new process for the synthesis of multilayered materials having a wide range of potentially useful engineering properties. Selection of molecular constituents and their incorporation into alternating bilayers allows control of electronic and optical properties useful for nanophotonic and nanoelectronic materials and devices. The nanostructure of the molecular materials in each layer further allows control over the electronic nature of the materials.

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6. ACKNOWLEDGEMENTS

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