Zinc-Bisquinoline Coordination Assemblies of High Refractive Index and Film Uniformity

D. L. Thomsen III, T. Phely-Bobin, and F. Papadimitrakopoulos*

Department of Chemistry, Polymer Science Program Nanomaterials Optoelectronics Laboratory Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269-3136

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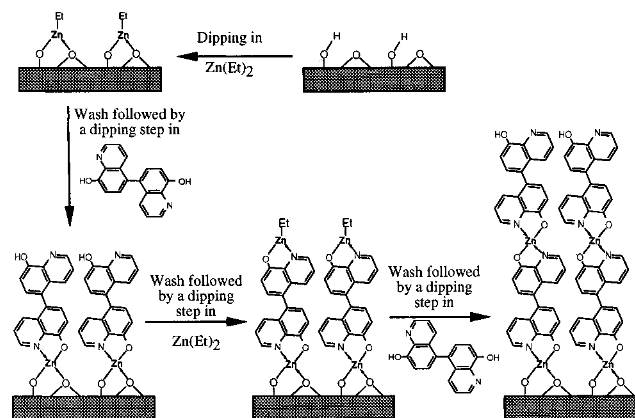
Thermal evaporation of low molecular weight organics permits the growth of uniform thin films, capable of producing controlled device heterostructures.[1] However, morphological changes during prolonged thermal treatments have led to interdiffusion, densification, and partial crystallization of layered structures that ultimately compromise device operation.[2−4] Polymers could potentially overcome such structural instabilities, although, current limitations in achieving high purity and device heterostructures comparable to small molecules have affected device efficiencies and lifetimes.[2,5] The introduction of self-assembly methods such as silanes,[6] disulfides,[7] thiols,[8,9] zirconium phosphonates,[10] and polyelectrolytes[11−13] have advanced considerably the manipulation and growth of low and high molecular weight organics at surfaces. In an effort to avoid the introduction of unconjugated moieties (such as ionic and silane groups) that could potentially increase electrical resistance, our laboratory has introduced a self-assembly process[14] which exhibits a high density of chromophores.

Scheme 1 illustrates the self-assembly process of diethyl zinc and 8,8′-dihydroxy-5,5′-bisquinoline (bisquinoline) resulting in films capable of electroluminescence.[15] We presently report that this methodology yields films of the highest reported index of refraction (n) for a solution-grown molecular self-assembly, $n = 1.69$ at 633 nm, and superb film uniformity over large areas, as measured by ellipsometry and atomic force microscopy. Such uniformities have allowed us to prepare single layer light emitting diodes, where films as thin as 400 Å resulted in working devices that were free from pinholes.[15] The resulting insoluble and intractable films of poly(zinc-bisquinoline)[16] assemblies[14] that are directly attached to substrates (of various surface topologies), along with the ability in growing complex layered structures, add to the novelties of this approach.

Scheme 1. Schematic Representation of the Self-Assembly Growth of Poly(zinc-bisquinoline)[a]



[a] This simplified illustration is further elaborated in the text.

Zinc-bisquinoline self-assemblies were grown in an inert environment on Si substrates coated with 19−20 Å native oxide. Alternative dipping, with 1−2 min intervals, in dilute THF solutions of $ZnEt_2$ and bisquinoline, with solvent washes between, constitute a dip cycle (d.c.).[14] Figure 1 illustrates this self-assembly as a function of number of successive dip cycles characterized by spectroscopic ellipsometry. A distinct two-stage growth rate occurs under these assembly conditions. Films thicker than 100 Å maintain the 26.5 Å/d.c. growth rate as far as we have measured (ca. 1275 Å). The 12.3 Å repeat of poly(zinc-bisquinoline), estimated from molecular simulations, indicates a controlled multilayer growth at stage II. The origin of this accelerated growth has been attributed to the association of diethyl zinc in anhydrous tetrahydrofuran, which can range from dimer to trimers.[17] Film swelling by $ZnEt_2$ and incomplete rinsing, might also contribute to an accelerated deposition, although are less likely to result in consistent growth rates and film-uniformity. In stage I, consistent with adsorbed water and oxygen on the native oxide surface of the silicon substrate, the first layer of deposition appears to be in the vicinity of 24 Å. X-ray photoelectron spectroscopy (XPS) concurs with a ZnO_x surface anchor layer, thicker than the monolayer coverage depicted in Scheme 1. Initial substrate roughness (which is in the order of 8.3 Å for polished Si substrates), varying surface coverage of anchor sites, and ellipsometric limitations associated with such topology are important parameters in considering the observed growth at stage I. Similar effects have been reported for other self-assemblies as well.[18] The increased multilayer growth and the gravimetric nature of zinc-bisquinoline[16] allow quick film preparations for such assemblies, (e.g., 1000 Å film in 5 h for an 8 min dip cycle).

The optical constants of poly(zinc-bisquinoline) assemblies were determined using a variable angle spectroscopic ellipsometer (VASE).[19,20] Seven films with thicknesses ranging from 1080 to 1275 Å[21] were measured at 60°, 64°, 68°, 72°, and 76° incident angles scanned between 600 and 1000 nm. The isotropic index of refraction *(n)* was calculated from the ellipsometric Psi and Del values at multiple incident angles, based on wavelength (λ) fit of the Cauchy dispersion model (1) and its constants A, B, and C, given below:

* To whom correspondence should be addressed.

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(21) *At 633 nm and 1.69 refractive index the Psi values pass through their maximum between 1080 and 1275 Å film thicknesses.*

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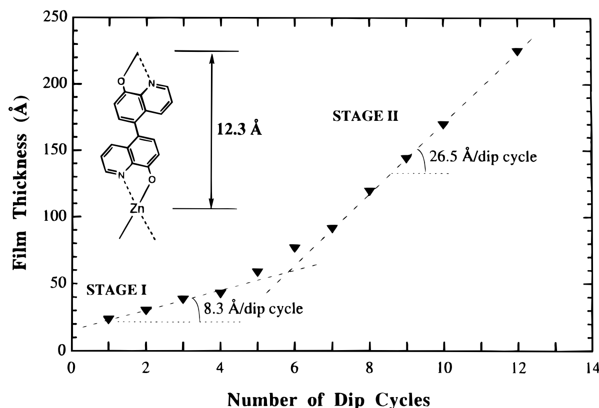

Figure 1. Ellipsometrically determined thickness versus dip cycle for the poly(zinc-bisquinoline) self-assembly process.

$$n(\lambda) = A + B/\lambda^2 + C/\lambda^4 \quad (1)$$

with $A = 1.5474 \pm 0.00864$, $B = 0.076763 \pm 0.00862$, $C = -0.0071004 \pm 0.00208$, mean square error (MSE) = 33.48. The resulting index of refraction ranges from 1.71 to 1.62 between 600 and 1000 nm and is $n = 1.69 \pm 0.01$ at 633 nm (He−Ne laser line). Figure 2 illustrates a Psi-Del trajectory plot at 633 nm, 70° incident angle, and 4 nm bandwidth for poly(zinc-bisquinoline), for samples' thicknesses ranging between 0 and 1275 Å. Upon overlaying the model trajectories for $n = 1.65$, 1.70, and 1.75, it is evident that the refractive indices of individual films remain fairly uniform over a wide range of thicknesses.[22]

Performance and lifetime of organic light emitting diodes are particularly sensitive to thickness variations over large areas. The macroscopic average and standard deviation for thickness of a representative 1.2 × 0.6 cm film at seven different locations was determined to be 1180 ± 16 Å, utilizing VASE with spot diameter of 2 mm. Atomic force microscopy (AFM) at the contact mode was used to observe local surface variations at micron sizes. Zinc-bisquinoline assemblies were found to be smoother than the original film-free substrates (see Figure 2 inset). The surface undulations (peak to valley) for a 90 Å thick film was 17 Å (surface roughness of 3.4 Å), where as the starting silicon wafer shows undulations of 74 Å (surface roughness of 8.3 Å). The observed film uniformity allows opportunities in creating a variety of heterostructure layered devices for optoelectronic applications.

Crystallinity was shown to greatly improve carrier mobilities and current densities in organic semiconductors.[23,24] Considerable amount of effort has been exerted to characterize the order in self-assembled monolayers and multilayers.[25] Self-assembled monolayers and multilayers of alkyl silanes,[26] alkanoic acids,[27] and thiols[8] have demonstrated order as a result of chain packing. In light of the fact that wide-angle X-ray diffraction of zinc-bisquinoline assemblies have not shown clear signs of crystallinity, refractive index correlation can provide sufficient insight of the molecular packing in such films.[20] Thin films, thick enough for accurate optical constant determination, can be directly correlated with bulk refractive indices.[25,28,29] Although oligomers of zinc-bisquinoline have shown crystallinity,[15,30] the optical constants of these materials have not been determined yet. At present, the closest analogue is the single crystal of zinc quinoline dihydrate which has a reported density of 1.68 g/cm^3 and refractive indices of $n_\alpha = 1.65$, $n_\beta = 1.78$, and $n_\gamma > 1.82$.[31] Even with the simple isotropic dispersion modeling of VASE spectra, these assemblies appear to be quite dense. To the best of our knowledge, the current index of refraction ($n = 1.69 \pm 0.01$) is the highest of the reported values of multilayer assemblies of conjugated chromophores. The measured bulk values of zirconium phosphonates (Zn is much lighter than Zr) appear to range between 1.52 and 1.54[10,32−34] where polyelectrolyte self-assemblies have shown refractive indices ranging from 1.47 to 1.60.[35] The achieved density and film uniformity[33,34,36] of these films demonstrate that such molecular self-assemblies can find a wide range of applications in optoelectronic devices.

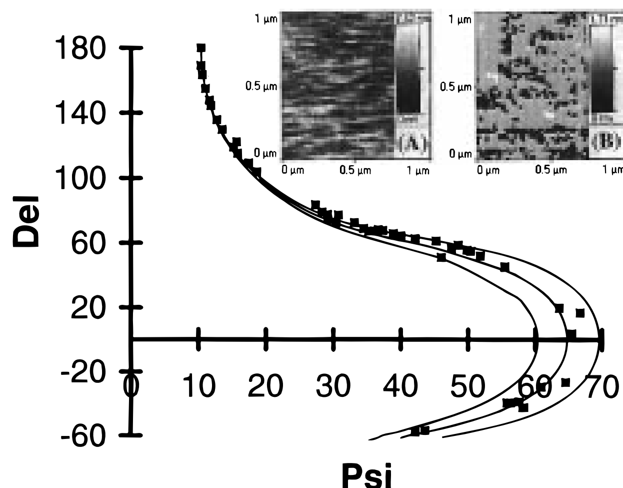

Figure 2. PSI versus DEL trajectory plot of poly(zinc-bisquinoline) films ranging in thicknesses from 0 to 1275 Å, at 633 nm and 70° incidence. From left to right the solid lines represent the model trajectories of $n = 1.75$, 1.70, and 1.65, respectively. Inset depicts the AFM surface topography of a typical (A) Si substrate and (B) a 90 Å thick poly(zinc-bisquinoline) film.

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