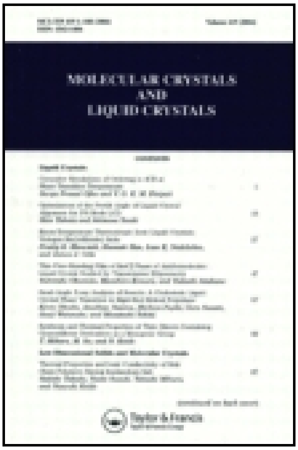

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Supramolecular Thin Film Architectures for Photonic Applications

Rigoberto Advincula [a] , Curtis W. Frank [a] , Daniel Roitman [b] , Jim Sheats [b] , Ron Moon [b] & Wolfgang Knoll [a c]

[a] Center on Polymer Interfaces and Macromolecular Assemblies, Department of Chemical Engineering, Stanford University, CA, USA

[b] Hewlett Packard Laboratories, Solid State Technologies Department, Palo Alto, CA, USA

[c] Max-Planck-Institut fur Polymerforschung, Ackermannweg 10, D-55128 Mainz, Germany, and Frontier Research Program, The Institute of Physical and Chemical Research (RIKEN), Wako-shi, Saitama, 351-01, Japan

To cite this article: Rigoberto Advincula, Curtis W. Frank, Daniel Roitman, Jim Sheats, Ron Moon & Wolfgang Knoll (1998): Supramolecular Thin Film Architectures for Photonic Applications, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 316:1, 103-112

To link to this article: http://dx.doi.org/10.1080/10587259808044470

Mol. Cryst. Liq. Cryst., 1998, Vol. 316, pp. 103–112
Reprints available directly from the publisher
Photocopying permitted by license only

Supramolecular Thin Film Architectures for Photonic Applications

RIGOBERTO ADVINCULA[a)], CURTIS W. FRANK[a)], DANIEL ROITMAN[b)], JIM SHEATS[b)], RON MOON[b)], and WOLFGANG KNOLL[a),c)]

a) Center on Polymer Interfaces and Macromolecular Assemblies, Department of Chemical Engineering, Stanford University, CA, USA
b) Hewlett Packard Laboratories, Solid State Technologies Department, Palo Alto, CA, USA
c) Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz, Germany, and Frontier Research Program, The Institute of Physical and Chemical Research (RIKEN), Wako-shi, Saitama 351-01, Japan

Abstract We report on the fabrication and characterization of electroluminescent devices based on a thin film preparation strategy that involves the alternate polyelectrolyte deposition from aqueous solution for the hole injection/ transporting layer combined with a conventional spin-cast method for the luminescent layer (MEH-PPV). Surface plasmon optical techniques are used to monitor the deposition process in-situ, as well as to quantify structural parameters of the final multilayer assemblies. These data are complemented by UV-vis spectroscopy, and X-ray reflectivity measurements. The final devices are functionally characterized in terms of their current-voltage, as well as their luminance-voltage performance.

Keywords: Photonics, Organic Thin Films, Alternate Polyelectrolyte Deposition, Electroluminescence, Polymer Light Emitting Devices

Introduction

Over the years, various schemes have been developed for the preparation of thin and ultrathin organic films for photonic and electronic applications. Some examples are depicted in Fig. 1 (a). The most simple one but, nevertheless, most successfully used in photoresist applications is the spin-coating of planar substrates by photo-reactive polymer solutions[1]. Here, films are prepared with thicknesses ranging from a few hundreds of nanometers up to a few micrometers. The employed polymer materials are typically in a glassy-amorphous state with no intrinsic order or orientation of the macromolecular chain segments or additionally introduced functional units.

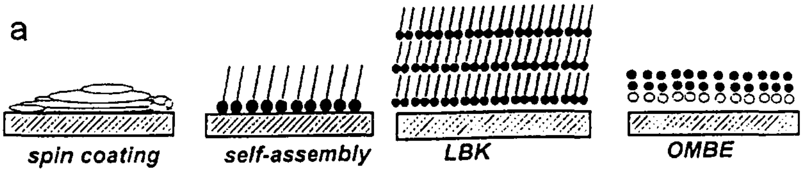

FIGURE 1 (a): Various thin film architectures.

The other extreme, i.e., thin films with a perfect crystalline order are prepared by organic molecular beam epitaxy (OMBE)[2]. This high vacuum preparation of thin films so far has been demonstrated for a limited set of organic systems only. Undoubtedly, the obtainable functional films bear a tremendous potential for the fabrication of photonic devices. At the moment, however, the preparation is extremely slow, suitable for certain materials only, and very costly. It can be expected, therefore, that this technique will be limited to very special cases, at best.

Another technique which also leads to films of a remarkable intrinsic organization and order was first described by K. Blodgett who transferred the monomolecular layers of amphiphilic molecules prepared by I. Langmuir at the water/ air interface, by simply dipping and withdrawing a solid substrate through such a monolayer, thus building multilayer assemblies whose thicknesses were controlled by the number of dipping cycles[3]. It was Hans Kuhn and his coworkers who demonstrated the immense potential of this preparation concept for the fabrication of functional supramolecular assemblies for future molecular electronic and photonic devices[4]. The method is hence called Langmuir/ Blodgett/ Kuhn (LBK) technique.

A similar approach is given by the self-assembly process[5]. Here, the specific interaction of a reactive headgroup with a corresponding substrate (e.g., silanes on oxide surfaces, thiols or disulfides on Au and Ag, -COOH on alumina) provides the gain in enthalpy required to overcompensate the loss in entropy upon the ordering of the long chain molecules during the formation of a highly organized monomolecular layer. Although mostly used for the functionalization of a solid surface by one single monolayer, e.g., in biosensors or for tribological applications, it has been demonstrated that a surface reaction of the endgroups of the assembled molecules also allows for the build-up of multilayer assemblies[6].

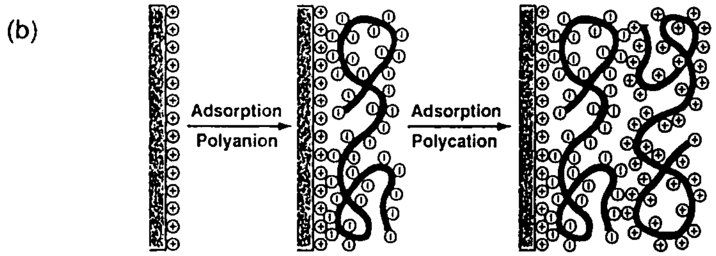

FIGURE 1 (b): The concept of alternate polyelectrolyte deposition for the fabrication of multilayer assemblies.

A most simple technique for the preparation of molecularly controlled thin organic films was recently introduced by G. Decher and coworkers[7]. A solid substrate with a charged surface, e.g. by the self-assembly of a suitable monolayer, is exposed to an (aqueous) solution of a polyelectrolyte carrying the corresponding counter-ions (cf. Fig. 1 (b)). The adsorption of some of these polymers leads to a thin coating with an overcompensation of the charge density thus leading to another interfacial charge layer, this time with the opposite sign. This surface, when exposed to an oppositely charged polyelectrolyte is again coated by a second polymer monolayer, such that when carried out sequentially, even thicker polymer coatings can be fabricated by this alternate deposition protocol. Basically, every charged (macro-) molecule or supramolecular unit can thus be organized resulting in highly structured (multi-) functional films[8] . Some of the advantages of this preparation method are i) the nearly unlimited range of materials that can be assembled ii), the molecular control of the film architecture at the Ångstrom level iii), the possibility to coat non-planar substrates, and iv) to generate lateral patterns.

In the following we briefly describe some of our efforts to use this preparation technique for the construction of electro-luminescent devices[9, 10, 11]. In particular, we demonstrate the performance of hole-transporting layers made from polyanilines (PANI) and sulfonated polyanilines (SPANI) in serveral different polyelectrolyte pairings.

The alternate polyelectrolyte deposition

Fig. 2 (a) displays the employed polyelectrolyte materials. The synthesis of the PANI and SPANI follows the procedures of MacDiarmid[12] and Epstein[13], respectively. The initially synthesized emeraldine hydrochloride was converted to emeraldine base by reacting with NH_4OH, ammonium hydroxide for 24 hours. The polymer can be made water soluble as a dilute solution by first dissolving it in DMAC, dimethylacetamide, 20 mg/ml and subsequent dilution 1:10 in water. Sulfonation of the PANI proceeded by reacting with fuming sulfuric acid and isolating the product which was very soluble in 0.1 M NaOH. The MW was estimated to be between 25,000 to 50,000 based on a similar literature procedure. All other materials were obtained from commercial sources.

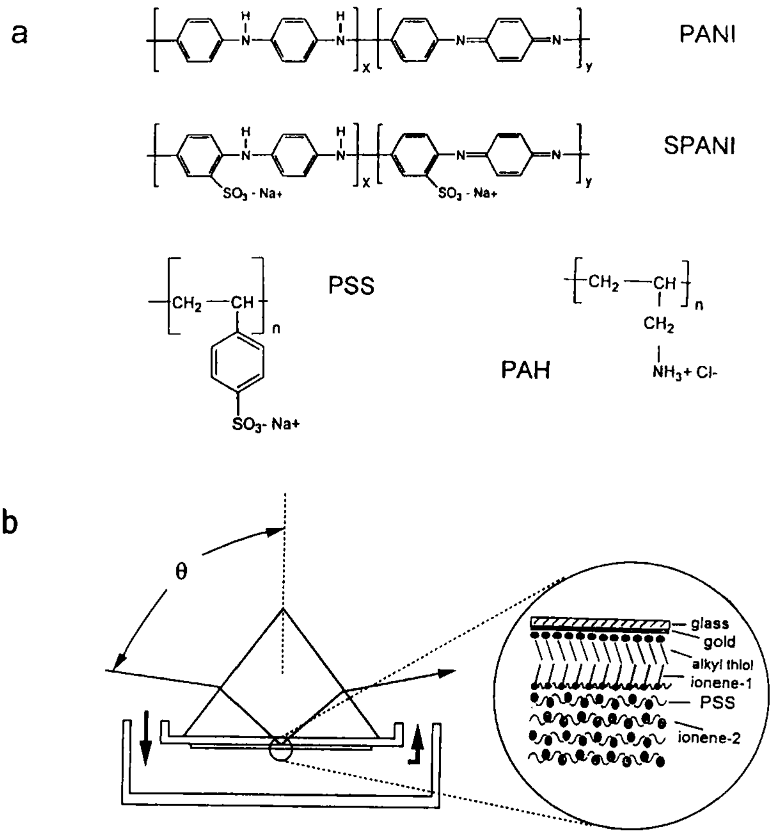

FIGURE 2: (a) Structure formulas of the employed materials. (b) Surface-plasmon optical set-up for the on-line monitoring of the multilayer formation.

A typical photolithographic PLED assembly involves the formation of a pattern of the luminescent polymer layer. A one layer device is based on the use of ITO as the anode, luminescent polymer (MEH-PPV, for example) as the active layer, and Ca or Mg as the cathode. In our case, a 2 layer configuration was used in which layers of SPANI or PANI were deposited over the ITO substrate prior to spin coating of the MEH-PPV which was capped by a Ca electrode.

As mentioned above, the polymer self-assembly solution adsorption involves the alternate deposition of oppositely charged polyelectrolytes. This procedure starts with the preparation of a uniformly charged surface on a solid substrate. Multilayer adsorption proceeds by creating a surface charge excess for each deposition. Washing is implemented between each deposition. In principle, parameters such as pH, concentration, salts, time of adsorption, polymer pair, etc. can be manipulated to control the deposition and final film properties.

The deposition process could be monitored on-line by surface plasmon spectroscopy[14]. The corresponding set-up is shown in Fig. 2 (b). The prism used in the Kretschmann-configuration for the resonant excitation of surface plasmons at the Au/ dielectric interface is directly coupled to a flow cuvette.

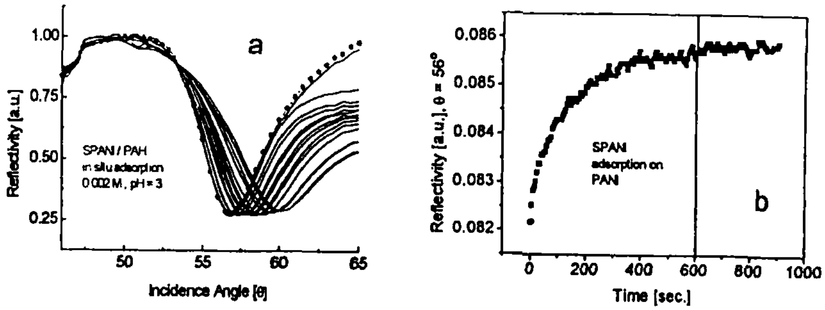

FIGURE 3: (a) Series of reflectivity scans taken after each polyelectrolyte layer deposition. (b) Kinetic data taken during the deposition of a layer of SPANI onto a PANI surface.

A liquid-handling apparatus allows for the sequential flow-through of polyanion-, polycation-, or pure buffer solutions while simultaneously recording the reflectivity of the interface in the total internal reflection geometry[15].

Two types of modes of operation are used: The angular reflectivity scan taken prior to or after each deposition step (cf. Fig. 3 (a)) allows for the quantitative determination of the adsorbed layer thickness. Required is an estimate of the refractive index of the polymer. The deposition process itself can be followed in a kinetic mode: The reflected intensity is monitored permanently at a fixed angle of incidence while the polymer adsorbs (cf. Fig. 3 (b)).

The thin film properties

After the completion of the multilayer formation, the sample is taken out of solution, rinsed and dried, and its structural and optical properties are further characterized.

The electronic transitions of the SPANI and PANI systems can be easily used to monitor by UV-vis absorption spectroscopy the layer thickness increase with the number of adsorption cycles. Another indication of the constant thickness increment per deposited polymer layer originates from the angular scans of surface plasmon spectroscopy taken in air. This is shown in Fig. 4 for the three systems SPANI/ PAH (cf. also the sequence of SPS spectra shown in Fig. 3 (a)), PANI/ PSS, and SPANI/ PANI. From the slope of the linear fit through the data points and the origin we deduce a monotonous deposition behavior with a double layer increment per polyanion/ polycation-cycle of 1.7 nm, 2.0 nm, and 2.5 nm for the three pairs, respectively. These values can be modified by assembling, e.g., from solutions of different polymer concentration, or by the addition of salts.

Additional structural data were obtained for the SPANI/ PANI and SPANI/ PAH mixed multilayers by X-ray reflectivity measurements (not shown). From the Kiessig fringes one obtained film thicknesses that were in quantitative agreement with the optical data.

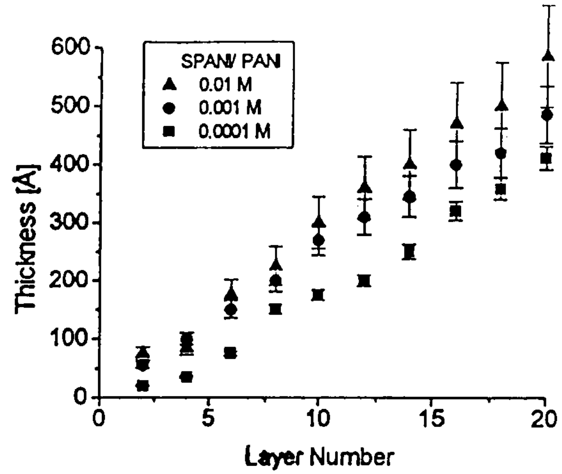

FIGURE 4: Thickness increase for SPANI/ PANI multilayers of increasing layer numbers, assembled from different concentrations.

The performance of the final electroluminescent device

In Fig. 5, initial results of the electroluminescent behavior of self-assembled layers in PLEDs is shown. In Fig. 5 (a), the comparison is made for the current-bias voltage (I-V) characteristics between, spin coated PANI doped with camphor sulfonic acid in m-cresol, self assembled PANI/ PSS and bare ITO. As can be seen, the modification of the ITO surface by either spin-coated PANI or self-assembled PANI results in a lower turn-on voltage and a more efficient current/ voltage correlation than for the bare ITO surface. The advantage of the self-assembled PANI over the spin-coated system is the

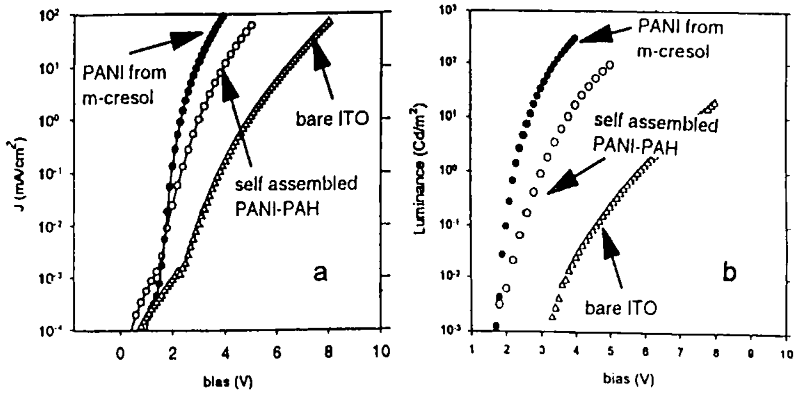

FIGURE 5: (a) Current-bias voltage, and (b) luminance-voltage characteristics for various electroluminescent devices.

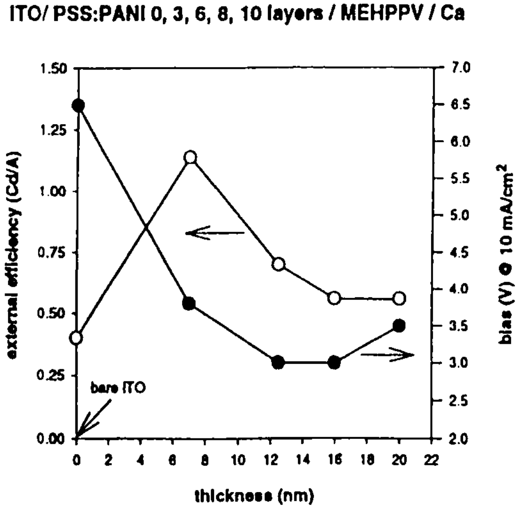

FIGURE 6: Bias Voltage and efficiency of a multilayer electro luminescent device with increasing thickness of the PANI/ PSS multilayers.

absence of pinhole defects observed in very thin layers. In our case, a 20 nm film only (10 double layers) is capable of significantly improving the efficiency. The luminance data for the same samples are compared in Fig. 5 (b).

Figure 6 gives an example for the variation of the electrical and optical properties of the final device as a function of the multilayer thickness. Obviously, several layers of PANI/ PSS are needed to fully develop the desired hole injection/transporting characteristics.

REFERENCES

1. Electronic and Photonic Applications of Polymers, M.J. Bowden and S. R. Turner, eds, Adv. in Chemistry Series 218, Am. Chem. Soc., Washington DC, 1988
2. T. Schmitz-Hübsch, T. Fritz, F. Sellam, R. Staub, and K. Leo, Phys. Rev., B 55, 7972 (1997)
3. M.C. Petty: Langmuir-Blodgett films, Cambridge University Press, Cambridge, 1996
4. H. Kuhn, D. Möbius, and H. Bücher, in: Physical Methods of Chemistry, A. Weissberger and B.W. Rossiter, eds., Part III B, Chap. VII, Wiley & Sons, New York, 1972
5. A. Ulman: Ultrathin Organic Films, Academic Press, San Diego, 1991
6. R. Maoz, J. Sagiv, D. Degenhardt, H. Möhwald, & P. Quint, Supramol. Sci., 1, 9 (1995)
7. G. Decher & J. D. Hong, Makromol. Chem. Makromol. Symp., 46, 321 (1991)
8. W. Knoll, Curr. Opinion Colloid Interface Sci., 1, 137 (1996)
9. A.C. Fow, O. Onitsuka, M. Ferreira, and M.F. Rubner, Mater. Res. Soc. Symp. Proc., 369, 575 (1995)
10. J. Tian, C.-C. Wu, M.E. Thompson, J.C. Hurm, R.A. Register, M.U. Marsella, and T.M. Swager, Adv. Mater., 7, 395 (1995)
11. H. Hong, D. Davidov, Y. Avany, H. Chayet, E.Z. Faraggi, and R. Neumann, Adv. Mater., 7, 846 (1995)
12. MacDiarmid et al. in: Conducting Polymers, L. Alcacer, ed., 1987, 105.
13. Epstein et al., J. Am. Chem. Soc., 112, 2800 (1990).
14. E.F. Aust, S. Ito, M. Savodny, and W. Knoll, Trends in Polymer Science, 2, 313 (1994)
15. R. Advincula and W. Knoll, Langmuir, 12, 3536 (1996).