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The topography of organic light-emitting diode-component functional layers as studied by atomic force microscopy

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The layer-by-layer roughness of organic light-emitting diode (OLED)-component functional thin films deposited from different solvents by a spin-coating method was studied using atomic force microscopy (AFM) facilities.

Organic electroluminescent (EL) devices are of both academic and practical interest as full-colour flat-panel displays.[1,2] Tang and Van Slyke[3] suggested a multilayer variant of OLED, and great efforts have been made in the main principles of OLED work. Multilayered devices consist of a cathode, an anode and a series of organic layers (emitting, charge-transporting and charge-blocking). The efficiency and stability of OLED operation depends not only on the structure of an EL cell, compatibility of energy levels of organic electrode materials and their characteristics (oxidation, thermal stability, charge transporting and film-forming properties[2,3]) but also on the quality of film surfaces and layer interface boundaries. The main problems of the development of long-lived and efficient EL devices include (i) a search for new emitting, charge-transporting and electrode materials with more advanced properties and (ii) a morphology improvement in their vertical stacked multilayer heterostructures.

A spin-coating method is often used in OLED fabrication;[4] recently, enormous efforts have been made in understanding and controlling the growth of spin-coating thin films of inorganic and organic materials.[5,6] Attention was focused on the influence of solution concentration and viscosity, spin speed and ramp acceleration on film thickness.[7] Modern microscopic and spectroscopic methods have been used to evaluate the morphology of spin-coated thin films.[6] Using atomic force microscopy (AFM) in a tapping mode, detailed topography information on thin films of deposited compounds can be obtained.[8]

The aim of this work was to search correlations between the roughness of films deposited and the nature of solvents used in a spin-coating procedure.[†] The surface roughness of PVC

[†] In spin-coating deposition experiments, a solution with a concentration of 5 g dm^{-3} was used; the speed of rotation was 2500 rpm. Solvents ($CHCl_3$, EtOH and THF) were purified by standard procedures.

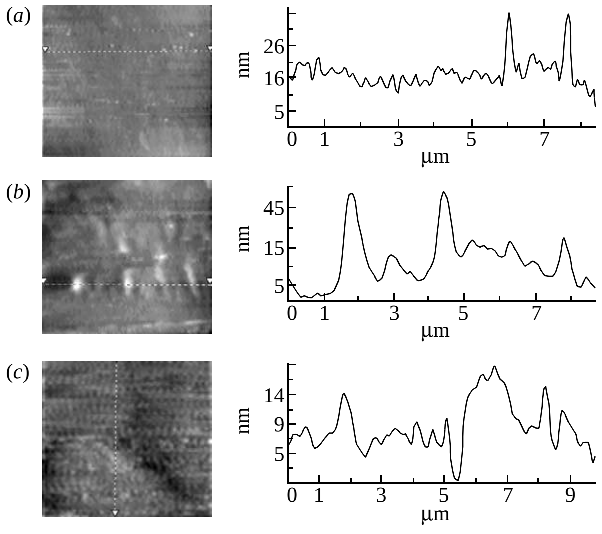

Figure 1 Cross-section profiles and AFM images of the surfaces of (*a*) ITO, (*b*) ITO/PVC–$CHCl_3$ and (*c*) ITO/PBD–$CHCl_3$.

(hole-transporting layer), PBD (electron-transporting layer) and $Tb(Sal)_3(TPPO)_2$ (emitting layer)‡ used in multilayer OLED structures[9] was studied layer-by-layer by AFM.§

The surface of commercial indium tin oxide (ITO) coated glass substrates is homogeneous with a roughness of 3 nm and imperfections of ~9 nm [Figure 1(*a*)]. The layers of transporting materials (PVC, PBD) deposited onto ITO from chloroform solutions (PVC–$CHCl_3$ and PBD–$CHCl_3$,¶ respectively) have similar surface profiles, but the roughness of an ITO/PVC–$CHCl_3$ layer [~11 nm, Figure 1(*b*)] is higher than that of ITO/PBD–$CHCl_3$ [~7 nm, Figure 1(*c*)]. The use of THF as a solvent instead of $CHCl_3$ results in the smoothing of ITO/PVC–THF and ITO/PBD–THF layers: the roughness values are equal to 5 nm.†† The above data are in good agreement with the facts that, in a spin-coating procedure, the morphology of organic thin films depends on the chemical nature of both compounds deposited and solvent used.[6]

The layers with different roughness (ITO/PVC–$CHCl_3$ and ITO/PBD–$CHCl_3$) served as intermediate layers for the deposition of an active one – $Tb(Sal)_3(TPPO)_2$ from EtOH and THF solutions.‡‡ The calculated values of roughness are given in Table 1, and the cross-section profiles of deposited layers are shown in Figure 2. Active layers deposited from an ethanol solution have higher roughness than the intermediate layers of both transporting materials PVC and PBD (Table 1, entries 1 and 4). The roughness of an ITO/PVC–$CHCl_3$/$Tb(Sal)_3(TPPO)_2$–EtOH layer is higher than that of ITO/PBD–$CHCl_3$/$Tb(Sal)_3(TPPO)_2$–EtOH. The observed increase in the roughness can result from the insolubility of PVC in EtOH and a low solubility of PBD in this solvent. The materials of intermediate layers are soluble in THF, and the topography of $Tb(Sal)_3(TPPO)_2$ emitting layers deposited from a THF solution is the same. The smoothing effect observed (Table 1, entries 2 and 5) arises from the solubility of transporting and emitting materials in THF, which may lead to layer interface smoothing. In contrary, multilayer structures with sharp interfaces between different vertical stacked materials require each material to be cast from a solvent in which the others must be insoluble.[4] However, in this case, the roughness of a following layer can increase in respect to that of an intermediate layer as it was observed for the ITO/PVC–$CHCl_3$/$Tb(Sal)_3(TPPO)_2$–EtOH structure (Table 1, entry 2).

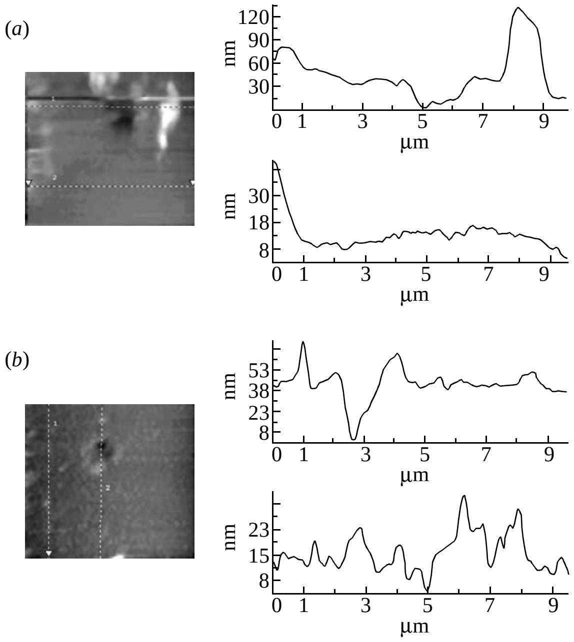

Figure 2 Cross-section profiles and AFM images in two different areas of surfaces for (*a*) ITO/PVC–$CHCl_3$/$Tb(Sal)_3(TPPO)_2$–EtOH and (*b*) ITO/PVC–$CHCl_3$/$Tb(Sal)_3(TPPO)_2$–THF.

The stability of OLED work can be improved with judicious selection of dopants in the host active emitting layer.[4] The co-deposition of transporting and emitting materials is often used in the fabrication of OLEDs with lanthanide coordination compounds as active layers.[10] The influence of the co-deposition of $Tb(Sal)_3(TPPO)_2$ with PVC or PBD§§ on the layer roughness was examined (Table 1, entries 3 and 6). The results show that the roughness of both of the doped layers are practically the same as that of $Tb(Sal)_3(TPPO)_2$–THF layers (Table 1, entries 2 and 5). In this case, the difference in the chemical nature and molecular weights of PVC and PBD has no influence on layer roughness.

In conclusion, a near-feild scanning optical microscopy (NSOM)/AFM technique can be effectively used for studying the morphology of OLED-component functional thin film layers. The roughness of layers deposited by a spin-coating method depends on the molecular weight of the materials, the solvent and the mutual solubility of materials forming vertical stacked layers in OLED structures. The influence of the layer morphology on the stability and efficiency of OLED operation requires a further study.

Table 1 The roughness of layers deposited.

Entry	Composition of layers deposited	Roughness/nm
1	ITO/PVC–$CHCl_3$/$Tb(Sal)_3(TPPO)_2$–EtOH	13
2	ITO/PVC–$CHCl_3$/$Tb(Sal)_3(TPPO)_2$–THF	9
3	ITO/PVC–$CHCl_3$/$Tb(Sal)_3(TPPO)_2$:PVC–THF	9
4	ITO/PBD–$CHCl_3$/$Tb(Sal)_3(TPPO)_2$–EtOH	9
5	ITO/PBD–$CHCl_3$/$Tb(Sal)_3(TPPO)_2$–THF	7
6	ITO/PBD–$CHCl_3$/$Tb(Sal)_3(TPPO)_2$:PBD–THF	8

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‡ The terbium complex with salicylic acid and triphenylphosphine oxide [$Tb(Sal)_3(TPPO)_2$] was prepared according to a published procedure.[9] ITO-coated glass (Delta Technologies, USA) was used as a substrate; the intermediate layers of PVC [poly(9-vinylcarbazol), Aldrich] – as the hole-transporting material, PBD [2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole, Aldrich] – as the electron-transporting material.

§ The morphology of thin films of obtained complexes was studied using a MoScan100 NSOM/AFM microscope in the contact shear-force distance control mode of AFM. For AFM manipulation and evaluation of the surface images, the ‘FemtoScan’ program package was used. The Roughness Command of this program calculated the mean square deviation of the height of different points on the surface from its average value $\sqrt{\sigma_z(x,y)}$ in the selected area or in its whole image. The standard deviation of roughness measurements is ±5%.

¶ Henceforth, ‘compound–solvent’ denotes the composition of a solution used for layer deposition.

†† The solubility of PVC and PBD in chloroform and THF is very high (more than 300 g dm^{-3}).

‡‡ $CHCl_3$ is not used because $Tb(Sal)_3(TPPO)_2$ is insoluble in this solvent.

§§ The weight ratios [$Tb(Sal)_3(TPPO)_2$]:[PVC] and [$Tb(Sal)_3(TPPO)_2$]:[PBD] were equal to 50:50, and the concentration of $Tb(Sal)_3(TPPO)_2$ in solutions was 5 g dm^{-3}.

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