

Surface roughness effects and their influence on the degradation of organic light emitting devices

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Organic light emitting devices typically consist of one or several organic layers which are sandwiched between two electrodes, one of which has to be transparent. In most cases indium tin oxide (ITO) is employed as the transparent, hole-injecting anode material. Usually, the functional organic layers possess a thickness of about 100 nm. For such thin films the homogeneity and the surface roughness are especially important factors for the device performance. Therefore, the surface roughness of all those layers which are the basis for subsequent deposition processes were systematically studied by atomic force microscopy (AFM). For these investigations both the ITO substrate and the layers consisting of different organic materials deposited onto the ITO substrate were analyzed. In addition, the two different basic deposition methods for the organic materials, namely the deposition from solution by spin coating and the deposition by thermal evaporation, were compared to one another with respect to their resulting surface roughness. It was found that the large surface roughness of the ITO substrate induces layer inhomogeneities, especially for the vapor deposited organic layers. They can be reduced by the incorporation of a polymeric smoothing layer. © 2000 Kluwer Academic Publishers

1. Introduction

Organic light emitting devices (OLEDs) receive considerable attention due to the high potential and advantages they can offer for flat panel technology. For instance, highly attractive low-cost and established deposition methods can be employed to obtain large-area displays and backlighting systems. Also, the independence of the viewing angle, as well as the availability of a broad range of colors are further promising aspects that contribute to the interest in this technology.

OLEDs usually consist of an organic single or multi-layer system sandwiched between two electrodes, one of which has to be transparent to allow the emission of light. Typically, indium tin oxide (ITO) is employed as the transparent, hole-transporting anode material. The cathode is made up of a low-work function metal or alloy.

In the meantime, very high luminances [1] and efficiencies [2] can be obtained already, which are entirely satisfactory for various technological applications. However, a major problem still remains the low life time which so far prevented the commercial use of such displays. Usually, a strong decrease of the electroluminescent intensity and the efficiency is observed during operation. In addition, the appearance of non-emitting areas (“dark spots”) is observed frequently, accompanied by an increase of the device-

resistance [3,4]. Therefore, the clarification of all degradation mechanisms is still of significant importance for establishing organic light emitting devices among flat panel displays.

In the literature several reasons have been identified to explain the observed degradation behavior. For instance, recrystallization effects within vapor deposited amorphous layers [5], insufficient electrochemical stability [3], or insufficient photostability [6] of the organic materials, as well as the oxidation of the cathode materials [7] are thoroughly discussed.

In this work further possible causes for degradation effects were examined. Specifically, effects related to the ITO electrode material and the surface properties of the substrate were of interest. Typically, the functional organic layers in organic LEDs possess thicknesses of about 100 nm. For such thin films the homogeneity and the surface roughness are especially important for reliable device performance. Therefore, the surface roughness of all those layers which are the basis for subsequent deposition processes were systematically studied by atomic force microscopy (AFM). For these investigations both the ITO substrate and the layers consisting of different organic materials deposited onto the ITO substrate were analyzed. In addition, the two different basic deposition methods for the organic materials, namely the deposition from solution (by spin coating)

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and the deposition by thermal evaporation, were compared to one another with respect to their resulting surface roughnesses.

2. Experimental

2.1. Materials

The glass substrates from Balzers were coated with ITO of about 100 nm thickness. Poly(vinylcarbazole) (PVK) is a hole-conducting polymer and was purchased from Aldrich. A substituted coumarin derivative (Makrolex 10GN, Bayer) was employed for the blend systems incorporating PVK as the matrix polymer. Polystyrene (PS, Aldrich) was the matrix polymer for a further blend system. For this blend system 1,3,5-tris[4-(di-4-ethylphenylamino) phenyl]benzene (TDAPB-4, AGFA) or aluminum tris(8-hydroxyquinoline) (Alq₃) were employed as the monomeric blend component. Aluminum tris(8-hydroxyquinoline) (Alq₃) was used as the model compound for the monomeric layers. It was synthesized by the reaction of aluminum trichloride (AlCl₃, Merck) with 8-hydroxyquinoline (Merck). For a further experiment poly(ethylenedioxythiophen polystyrenesulfonate) (Baytron P, Bayer) was employed as a hole-injecting layer spin-coated on the ITO substrate.

2.2. Preparation of the samples

The 2 in × 2 in ITO substrates were thoroughly cleaned by a detergent solution and deionized water, in combination with ultrasonification and a plasma-etching treatment prior to use. The polymeric blend systems were deposited under nitrogen by spin coating from a filtrated 1 wt-% solution of PVK : 10GN (mass ratio 4 : 1) or PS : TDAPB-4 (mass ratio 1 : 1) in 1,2-dichloroethane. The blend system PS : Alq₃ was spin coated from a 1 wt-% solution in tetrahydrofuran (THF). The monomeric Alq₃ was vacuum deposited by thermal evaporation in a vacuum below 10⁻⁵ mbar. Typically, the deposition rate was between 0.1 and 0.5 nm/sec.

2.3. Atomic Force Microscopy (AFM)

The topography surface roughness and material contrast, respectively, of the substrates were determined with Park Scientific Instruments (PSI Autoprobe CP) and Digital Instruments (Dimension 3000 with Nanoscope III controller) atomic force microscopes. With both atomic force microscopes quantitative surface analysis with resolution in the nanometer regime in all three dimensions is possible. The Digital Instruments Dimension 3000 microscope provides phase detection [8] yielding material contrast information. Silicon cantilevers with integrated tip (Nanosensors Pointprobe), spring constant of 20–40 N/m and resonant frequency of 280 kHz were used for tapping mode imaging. The PSI Autoprobe CP was used in contact mode with a titanium nitride tip (PSI-Microlever, radius about 50 nm) at a bearing force of about 0.5 nN.

3. Results

3.1. ITO substrate

ITO deposited onto a glass substrate is the basis for the deposition of the organic layers. Therefore, its surface properties are especially important for the device characteristics. The surface roughness of a cleaned substrate coated with ITO (Baltracon 255, Balzers) was measured by AFM. Fig. 1 shows the topographical image of a 5 μm × 5 μm area of this substrate surface. The grained structure of the surface is clearly recognizable. The root-mean-square (rms) roughness for this area is 2.7 nm, and the maximum peak-to-valley reaches 21.0 nm. In addition, island structures with lateral extensions of about 0.1 to 1 μm on the surface can be seen in Fig. 1. The enlarged sector is shown in Fig. 2 and clarifies these observed structures. Marked by an arrow in the front left area such a plateau exhibiting a sharp edge can be recognized. It stretches from the right front to the center back. The difference in height of the edge is about 7 nm. The fine structure of the islands shows grains which are about 20 nm in size and which possess the same maximum difference in height of 7 nm. It is noticeable that within the island the single grains seem to be grown together, whereas outside these plateaus larger single grains of about 40–60 nm can be found. This value correlates very well with the ones found in the literature [9] for tin doped In₂O₃ samples.

3.2. Polymer layer deposited on ITO substrate

Fig. 3a shows the surface of the blend system PVK and 10GN (mass ratio 4 : 1), as an example for the roughness of a polymeric system. The thickness of this layer is about 100 nm, and it was spin-coated at 400 rpm at room temperature from a 1 wt-% solution in 1,2-dichloroethane onto an ITO substrate. By AFM the surface of this layer appears almost completely unstructured. The homogeneous layer possesses a rms roughness of 1.0 nm, and the maximum difference in height (peak-to-valley) is about 9 nm. This value for the peak-to-valley is in good agreement with the differences in height which appear at the edges of the islands on the ITO surface.

The smoothing effect was observed independently from the matrix polymer and the blend molecule for all investigated polymer systems. Similar results were obtained, for instance, for the polymeric blend system PS : Alq₃ (mass ratio 1 : 1) spin coated from a 1 wt-% solution in THF onto the ITO substrate or for Baytron P. The AFM phase contrast images in Fig. 3b and the topographic linescans in Fig. 3c compare an ITO-Substrate (left image and linescan) with an 50 nm thick Baytron P layer spin coated onto ITO (right image and linescan). The phase contrast images of the uncovered ITO surface (Fig. 3b, left) clearly show a sharp contrast between single ITO grains and the surrounding grain boundary region. This contrast vanishes on the Baytron P coated ITO surface (Fig. 3b, right). This indicates that both the ITO grains boundary regions are filled and the ITO grains are completely covered with Baytron P. This conducting polymeric coating,

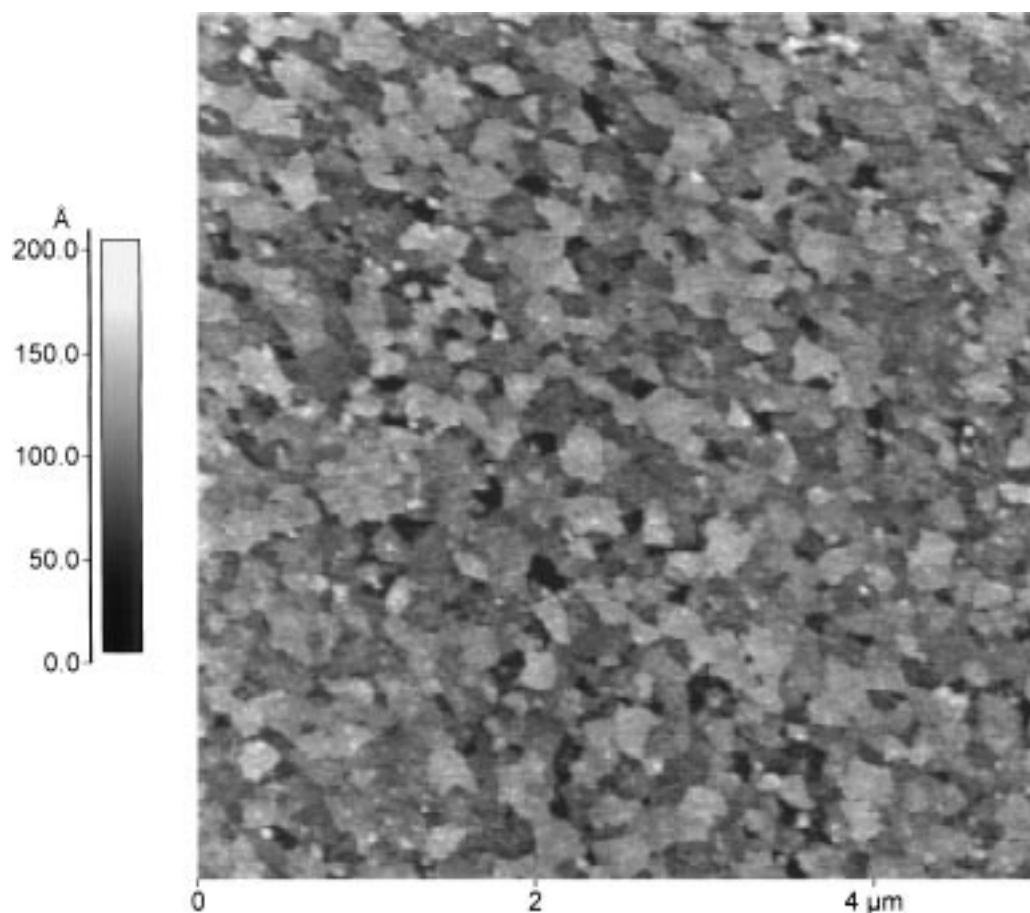


Figure 1 Topographical image ($5\ \mu\text{m} \times 5\ \mu\text{m}$) of a non-coated ITO substrate (Baltracon 255, Balzers).

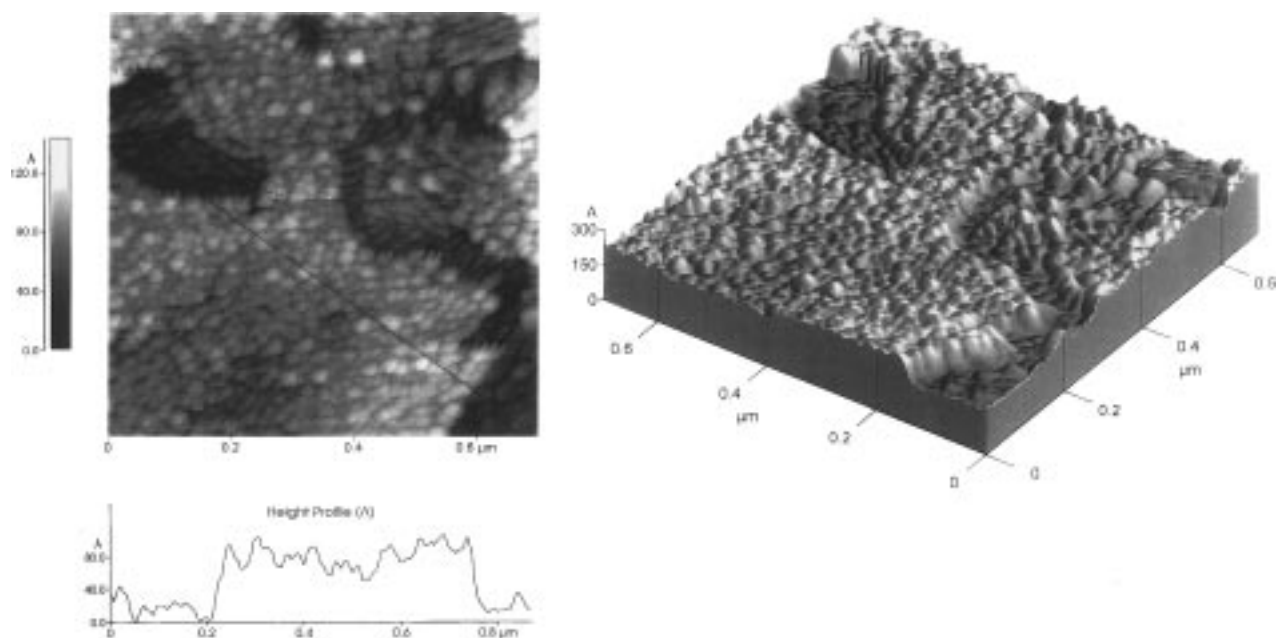


Figure 2 Relief topographical image ($0.7\ \mu\text{m} \times 0.7\ \mu\text{m}$) of a non-coated ITO substrate (Baltracon 255, Balzers).

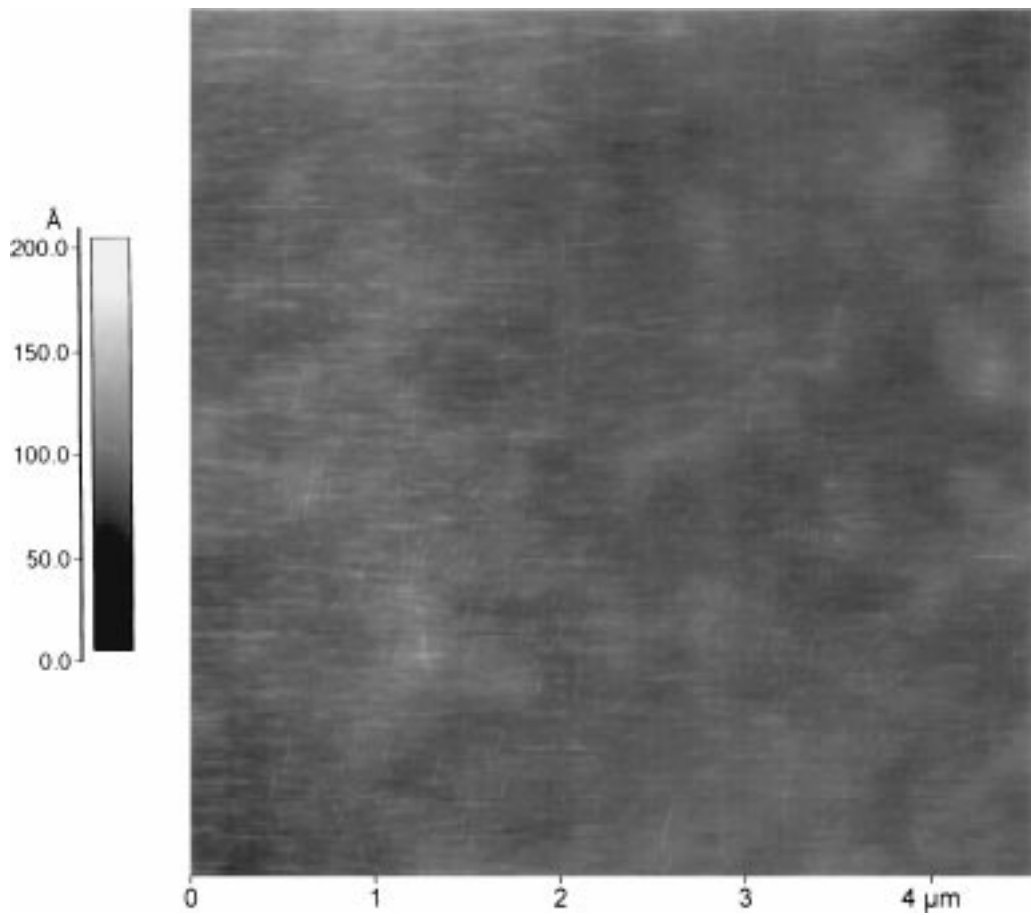
with excellent hole-injecting properties [10], reduces the roughness (peak to valley) of the uncoated ITO from about 10 nm (Fig. 3c, left) to about 3 nm (Fig. 3c, right). This material, often named “PEDT”, is also known to improve substantially the lifetime stability of polymer LEDs [11,12].

It is still necessary to clarify for which layer thickness the smoothing effect occurs. No change of the rough-

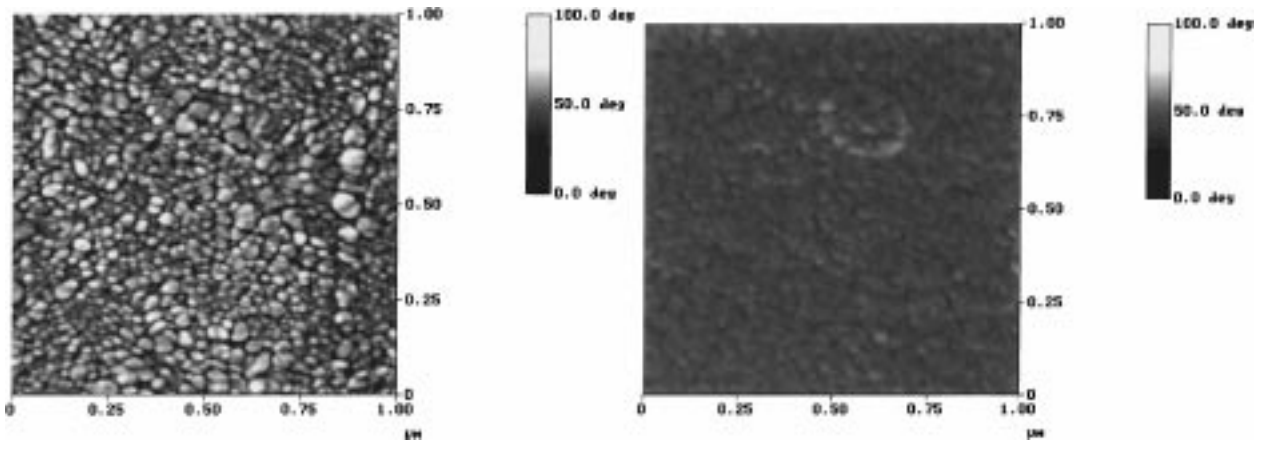
ness was observed over a time period of two months and storage in air at room temperature.

3.3. Monomeric layer deposited on ITO substrate

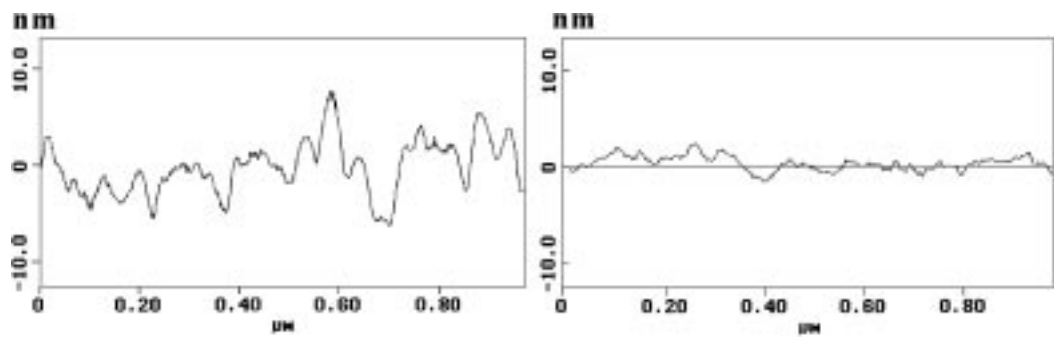
For the determination of the surface roughness of a vapor deposited monomeric layer Alq₃ was chosen as



(a)



(b)



(c)

Figure 3 (a) Topographical image ($4.5 \mu\text{m} \times 4.5 \mu\text{m}$) of an ITO substrate coated with a polymeric blend system PVK + 10GN (mass ratio 4 : 1). (b) AFM phase contrast images ($1 \mu\text{m} \times 1 \mu\text{m}$) and (c) topographical linescans of ITO (left) and a 50 nm Baytron P layer on ITO (right).

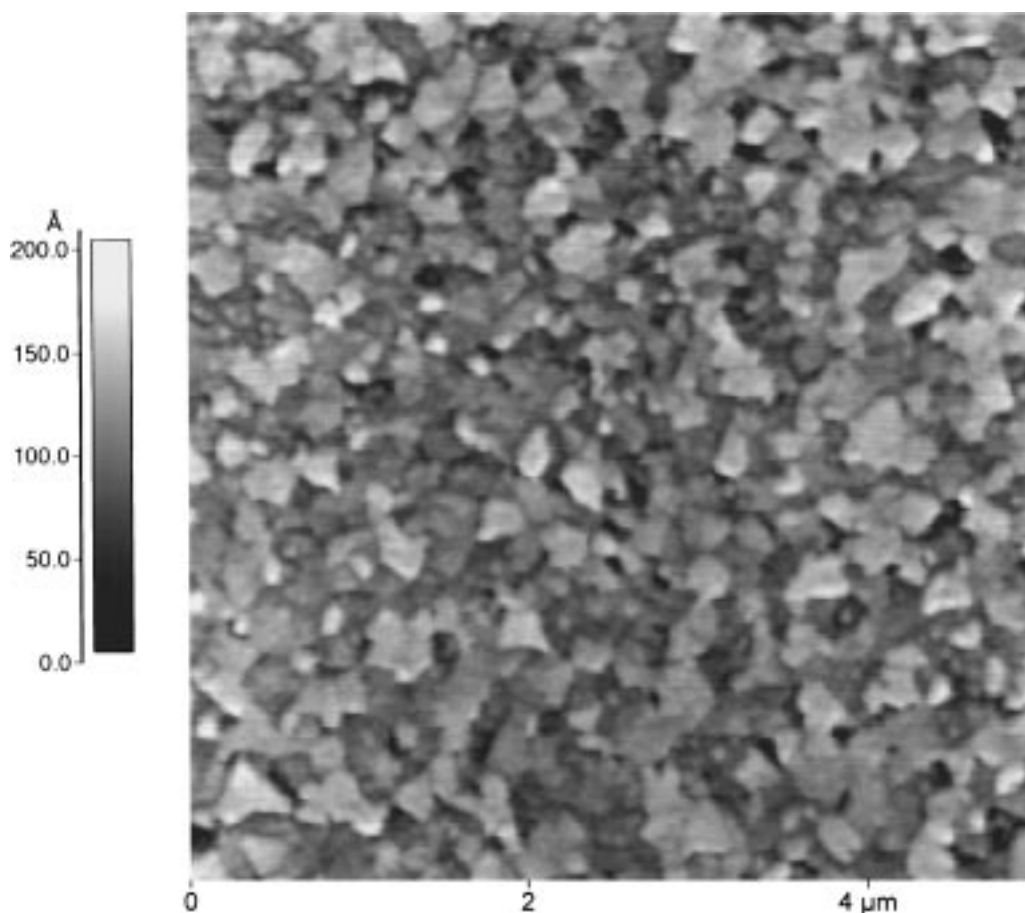


Figure 4 Topographical image ($5\ \mu\text{m} \times 5\ \mu\text{m}$) of an ITO substrate coated with monomeric evaporated Alq₃.

model compound. A 70 nm layer of this compound was vapor deposited onto the ITO substrate at room temperature and at a pressure below 10^{-5} mbar with a rate below 2 nm/s. The vapor deposition resulted in a closed layer of Alq₃ on the ITO substrate. From the micrograph shown in Fig. 4 it can be seen that a surface structure similar to the one for the uncoated ITO substrate is found. The rms roughness gives the same value of 2.7 nm, and the maximum difference in height in the investigated area even shows a somewhat higher value of 23.7 nm. After a two-week storage in air and at room temperature the sample did not show any changes in its surface roughness.

3.4. Monomeric layer deposited onto a polymeric layer

A monomeric layer of Alq₃ was vapor deposited onto an ITO substrate coated with PVK. The purpose was to evaluate the influence of the surface roughness of the polymeric film on the surface roughness of the vapor deposited monomeric layer. For this sample the surface of the monomeric layer clearly appears to be more homogeneous, as can be seen from Fig. 5, in contrast to the layer vapor deposited onto the non-coated ITO substrate (Fig. 4). This smoothing effect results in a reduced rms roughness of 1.2 nm, and the observed peak-to-valley value of 10.4 nm is comparable to the one shown by the polymeric layer (Fig. 3). Also for this sample no change in roughness could be detected after the storage for two weeks in air and at room temperature.

For a comparable sample (ITO/PS+TDAPB-4 (mass ratio 1 : 1)/Alq₃) a higher magnification ($260\ \text{nm} \times 260\ \text{nm}$) of the phase contrast image reveals an even, slightly undulating structure of the Alq₃ surface. The image is depicted in Fig. 6. The comparison of the calculated hexagonal habits of an Alq₃ crystal with the shape of this surface structure indicates the presence of Alq₃-microcrystals. The proposed Alq₃ habits are based on attachment energy calculations using Dreiding force field simulation (Cerius 3.5, Molecular Simulations). From the regularity of the phase contrast image an average grain size of about 80 nm is extractable, in good agreement with reported grain sizes obtained for sublimated Alq₃-layers [13, 14].

4. Discussion

Fig. 7 shows the frequency distribution of the height levels for the samples described above, which were found for every single pixel during the AFM measurements. The maximum of the distribution is assigned to zero. Thus, the half widths of the curves are a measure for the surface roughness. A broader distribution is equivalent to a higher surface roughness. This figure documents the two different distributions in surface roughness found. The uncovered ITO exhibits peak-to-valley differences up to 7 nm, compared to less than 3 nm for the ITO-substrate coated with the polymer.

The reduction of surface roughness is a common feature for all polymer layers investigated above. We

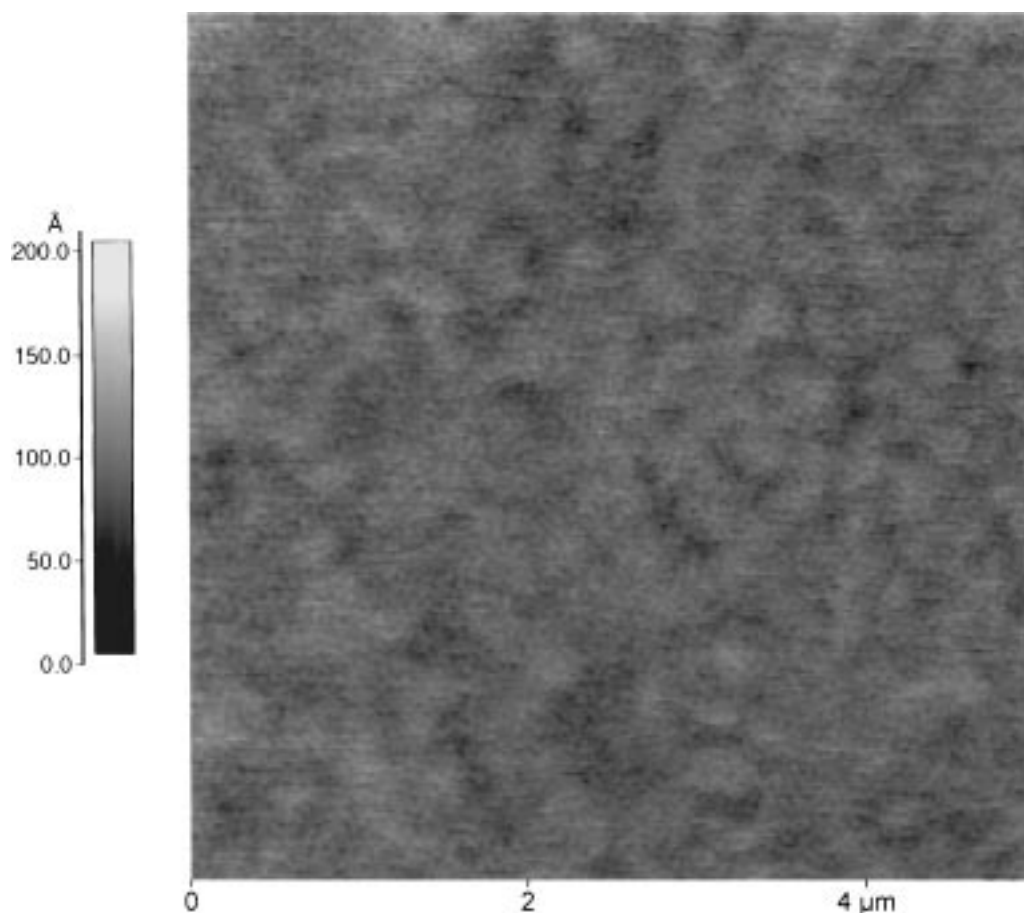


Figure 5 Topographical image ($5 \mu\text{m} \times 5 \mu\text{m}$) of an ITO substrate coated with PVK and subsequently vapor deposited Alq3.

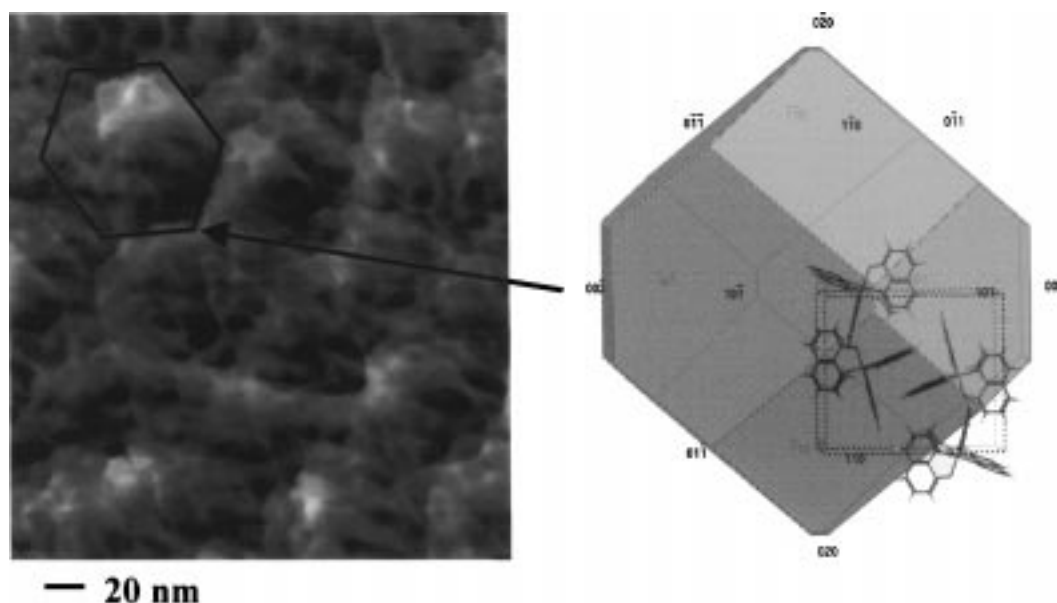


Figure 6 Phase contrast image ($260 \text{ nm} \times 260 \text{ nm}$) of the evaporated Alq3 surface deposited on a polymeric blend system (PS + TDAPB-4 (mass ratio 1 : 1)) (left). For comparison: calculated habits of an Alq3 crystal and inserted the unit cell of Alq3 (right).

find that the surface smoothing of ITO has important consequences for the performance of organic LEDs. Especially if a good hole-conducting polymer is spin-coated onto ITO this treatment leads to a reduction of electrical shorts. For organic LEDs which are entirely built up from monomeric layers, short circuits are frequently found under operation [13]. We can confirm these findings with experiments where a 50 nm thick

Alq3-layer was evaporated directly onto ITO. It was impossible to obtain stable I/U -characteristics with these devices. However, with an additional hole-injection layer such as Baytron P or PS/TDAPB-4, the occurrence of electrical shorts was drastically reduced.

When a supplementary layer or layer stack is deposited onto a polymeric intermediate layer the field strength-inhomogeneities will be reduced. Field

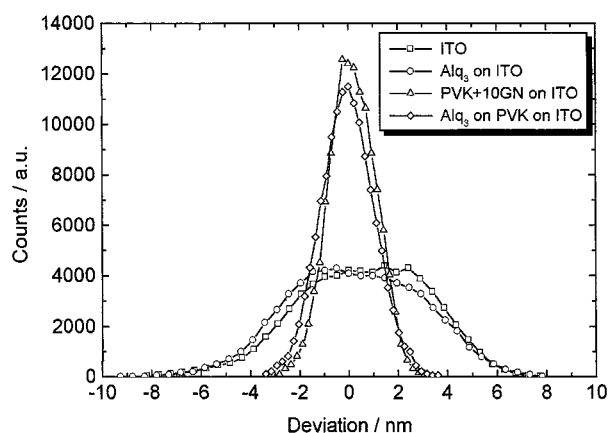


Figure 7 Frequency distribution of AFM topographic height levels of the single pixels for the ITO substrate and different layers on the ITO substrate. The maximum of the distribution is assigned to zero. A broader distribution means a higher roughness of the surface.

strength-inhomogeneities are present in case of variations of layer-thicknesses. Therefore, thickness-inhomogeneities have to be avoided, particularly within the layer where the voltage drop within the device is dominant. Following Fig. 7 the thickness-inhomogeneities of a 50 nm supplementary layer will be reduced by introducing a hole-injecting layer such as PS/TDAPB-4 from 14% to 6% of total layer thickness.

Additionally the smoothing of the ITO-surface by a polymeric layer should simultaneously reduce the inhomogeneous nucleation of evaporated crystallizable layers, i.e. Alq₃. The width of the crystal-size distribution will narrow, leading to fewer inhomogeneities in particle-sizes and grain-boundaries.

The areas within which a higher current is transported due to the higher field intensity, do not cause short circuits immediately after applying a voltage, but they exhibit bright spots ("hot spots") during operation. Due to the larger, locally-limited charge transport during operation they clearly suffer from an accelerated degradation during which they transform into non-emitting areas ("dark spots"), or they cause short circuits. Such probabilities for the occurrence of short circuits were also observed for vapor deposited multi-layer systems, for example TPD/Alq₃ [15]. Therefore, it can be assumed that such layer-inhomogeneities which were found here for the example of Alq₃, are a general property of monomeric layers vapor deposited onto an ITO surface. Polymeric layer systems, however, which can be deposited from solution, possess very smooth surfaces or interfaces, and exhibit a much lower dependency on the substrate roughness. More homogeneous layer properties result in a drastically reduced probability for short circuits with the first application of a voltage. Similarly, the so-called "hot spots" are found less often. The same effects were also found for monomeric systems which were vapor deposited onto a polymeric intermediate layer.

5. Conclusions

It was found that the large surface roughness of the ITO substrate induces layer inhomogeneities, especially for the vapor deposited organic layers. They can be reduced

by the incorporation of a polymeric electric contacting smoothing layer. As a result the current density is distributed homogeneously over the entire device area. Microscopic channels which suffer from accelerated degradation due to the higher locally-limited charge transport are not formed, and therefore short circuits, hot spots, and dark spots can be prevented or drastically reduced.

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