Algorithmic presentation of light-sensitive layers printing monitoring in-process

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Abstract. In the study the in-process monitoring algorithm for the flexible printed LED-pixels production at the light-sensitive layers formationstage is presented. The light-sensitive layers are based on either polymethine dyes complexes or luminophores. The both chemical and electrostatic interaction between the light-sensitive compounds and the bottom functional layer affected on crystallization conditions as well as the previous layer relief and thermal postprocessing parameters including next layers formationare most significant production factors. The production layers defects are determined. The optimal stages of optical properties monitoring are defined. The in-process optical properties monitoring technique is offered.

1. Introduction

The key production stage of the complex flexible thin-film multilayers systems aimed at capacity providing of the end printed electronics product (PEP) is formation and parameters monitoring of the so-called active layers – light-sensitive (light-emitting or absorbing) semi-conductive (for photovoltaic area) [1, 2], bioactive (for biosensors production) ones [3, 4] and etc. Depending on PEP-intending the active layers number can be varied from the only one – in case of monochrome elements (solar cell batteries, wide-format lighting, etc.) [5, 6] or bioelements (e.g. glucometers) [7] to three basic ones with selective electromagnetic absorbing in three visible spectrum ranges - R (red), G(green) and B (blue)in the full-color CCD-sensors [8]. On the other hand, there are known examples of one-layer compound mixing which are sensitive in different spectrum ranges [9] or their parallel partitioning in the same plane [10].

One of the known organic compounds for PEP-light-sensitive layers (LSL) is polymethine dyes (PD) [11] and their metal complexes [12] with ability to J-aggregation [11, 13] – molecular crystallization caused the narrow intensive absorption peak appearance shifted to long- or shortwave spectrum ranges depending on the dye type [14]. Other wide studying LSL-base materials are quantum dots [15, 16], perovskite and its functional compounds [17, 18], different inorganic luminophores [19], Alq3 [20, 21] and etc.

The general technological problems of PD-based LSL are both J-aggregation condition assurance and monitoring on a transport or/and conductive PEP-layers (the preferred crystallization direction at the molecular slip angle from 19 to 30°) [13].

Herein the any LSL-printing composition (LSL-ink) is the complex function of the LSL-molecules, solution and polymer matrix interaction accompanied with its multi-contacting between working element surfaces of a printing device (ink transfer system elements, printing plates, etc) and finally resulting in an engagement with bottom functional layer cooperation at the LSL-compounds crystallization procedure [13, 22]. As the result all above mentioned factors limit to a great extent both the techniques and parameters of LSL-printing. It should be noted, it is true for any active (functional) printing composition to the same degree. It is important to note that stability and LSL-composition parameters monitoring through time as well as at the environment changing (temperature, relative humidity, mainly) are no less significant.

The general organic LSL-compositions disadvantage is low light stability as a result of their interaction with singlet oxygen caused the LSL-molecules fracture [23]. Both final organic PEPs stability increasingand their production improvement can be solved by metal complex dyes application [24].

So, the quality control system of the multilayer PEPs printing process, its technical and metrological supporting at theLS-layers formationstage are connected with in-process monitoring difficulties of LSL-printing compositions properties at the both continuous highspeed printing and discontinued one (aimed at a layer full curing) due to theneed for numerous parameters monitoring and their variability at the LSL-compositions or printing technique changing.

2. Problem statement

It is known about such analyse methods of active layers quality as AFM crystal parameters monitoring [25], SEM layer morphology analysis accompanied with EDS [26, 27], spectrophotometry [28], XPS-profiling [25] and etc. at the layers formation process by lithography [29], dipping [30], coating [30] as well as ink jet [31, 32], aerosol jet printing [33] and other methods [32, 34–36].

The common points of the listed monitoring techniques are technological process stoppingrequirement, samples batch procedure and high-costanalysis resulted in valuable information massive which is important at the both research and preproduction startup stages whereas at the production the automated in-process monitoring based on effected factors control, both production defect determination and classification as well as testable equipment is demanded.

The study is targetedat thein-process quality monitoring algorithm development of the PEP light-sensitive layers production stage. The article is the logical extension of [37].

3. Methods and materials

The monochrome printed LED-pixels (II PEP type [37]) with LS-layers based on PD, their metal complex compounds and commercial available luminophores were produced on PET polymer films, glass with ITO coating by the various production methods application at the different PEP layers formation stages: dipping (the process described in [38, 39]), electrochemical deposition [40], screen, flexographic and aerosol jet printing [31-36] (figure 1).

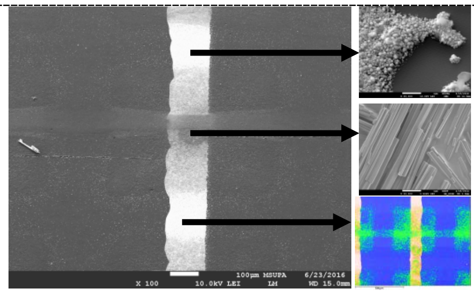

Figure 1. SEM – image of the printed pixel with EDS-mapping (right below)

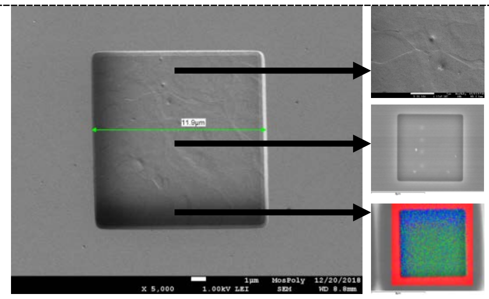

Figure 2. SEM – image of the commercial produced matrix pixel with EDS-mapping (right below)

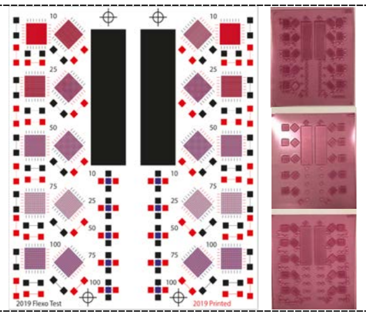

Figure 3. Scheme and photos of the test flexographic plates for roll-to-roll functional layers production

Both commercial available and developed functional silver-, carbon-containing printing inks and compositions as well as PEDOT:PSS and ZnO solutions were tested as conductive and transport (buffer) layers. The pixels were layer-by-layer characterized using FE-SEM (Jeol JSM 7500F) equipped EDS-detector Oxford X-Max-80, TR-200 profilometer, SF-2000 and X-Rite SpectroEye spectro(photo)densitometers. The commercial produced CCD-pixels structure was analyzed aimed at quality performance comparison (figure 2).

The printing plates with various initial technical parameters (described in [41]) based on the developed test-layout (figure 3) were examined for both the selection rationale and printing techniques combination practicability at the PEP production based on defects determination affected on LSL and, respectively, final PEP capacity.

4. Results

The printed pixels drastically defer from commercial produced by lithographic techniques due to both much higher geometrical equivocating of all pixel elements,which is inherent to a considerable degree for LSL because they are formed on chemically and structural different matrix elements, and LSL-crystal distribution inhomogeneity at all three dimensions increased by the bottom layer relief (figure 1, 2). The general trigger of all listed disadvantages is unstable layer-by-layer compositions application procedures from viscous fluids.

As expected, the basic monitoring LSL parameters are optical properties. In the previous study [37] the input parameters arrayed data of the developed in-process quality monitoring algorithm, depended on PEP configuration and layers succession type,is presented, where LSL-spectrum operationalrange was implemented as the both functional materials(placed on either side of the LSL) selection and their properties monitoring criterium (transparency inside the demanded ranges). The additional input parameters of the LS-layers quality monitoring algorithm are listed in table 1.

Table 1. Input parameters at the LSL-application stage

	Parameter	Symbols, measurement units
1	Reflection / absorption basic peak position of crystal LSL-compound	λb_i, nm
2	Full width athalf-height of the basic absorption peak / tolerance	FWHM, nm
3	LSL number	M_a, m
4	LSL thickness / tolerance	Da_j, m / Δ Da_j, m
5	LSL application scheme	Vertical / parallel (horizontal)
6	LSL-compound crystallization velocity / tolerance	υ_j, m/s / $\Delta\upsilon_j$, m/s

The absorption (reflection) basic peak position of crystal LSLindicates LSL-compound capacity for photoconductivity (“exiton” generation, in case of PD application) as a result of photons absorption with the specific energy.At the basic spectrum peak shifting as well as in case of additional peaks appearance – markers of other crystallization / aggregation forms, respectively, as it is typical for H-aggregation and so-called “monomer”, amorphous PD form) –the LSL effectiveness (quantum efficiency) is degreased. The full width at peak half-height (FWHM) is also one of the important performance capabilities points: its value depends on “LSL-compound – the bottom layer” interaction and indirectly reflects LSL-crystalssize distribution.

Based on above mentioned points it was practically defined that key factors of LSL formation with spectral controlled demanded optical parameters are:

1. Relief, homogeneity and surface energy of the bottom layer (figure 1, 6);
2. Chemical and electrostatic interaction between neighbouring layers, depended on LSL-compound crystallization conditions (figure 1, 4, 5);
3. Thermal processing conditionsof LSL, including all subsequent functional layers (figure 7)

According to the experimental results the crucial role of used printing technique parameters for LSL-crystallization was defined.

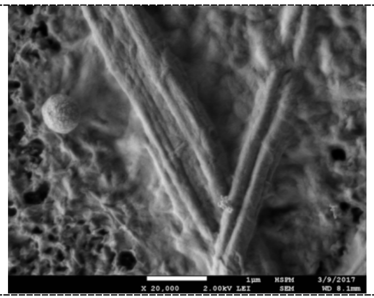

Figure 4. LSL crystallizing defect (H-aggregates presence)

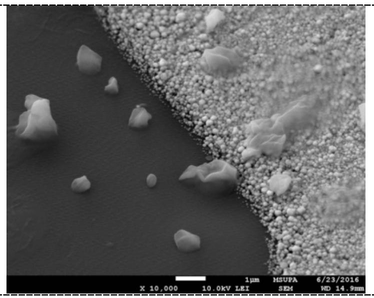

Figure 5. LSL crystallizing defect (monomer form presence)

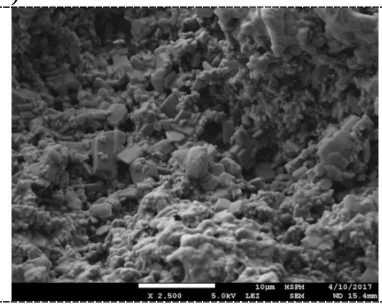

Figure 6. LSL relief defect

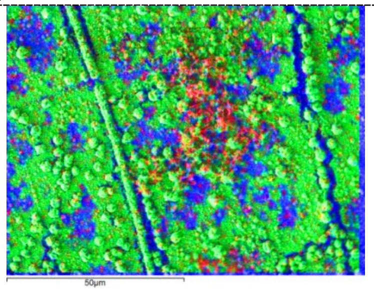

Figure 7. LSL breaking defect

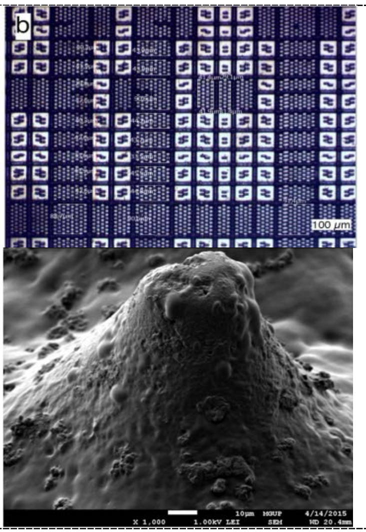

Figure 8. Flexographic printing form defects (optical photo (up) and SEM-image (down))

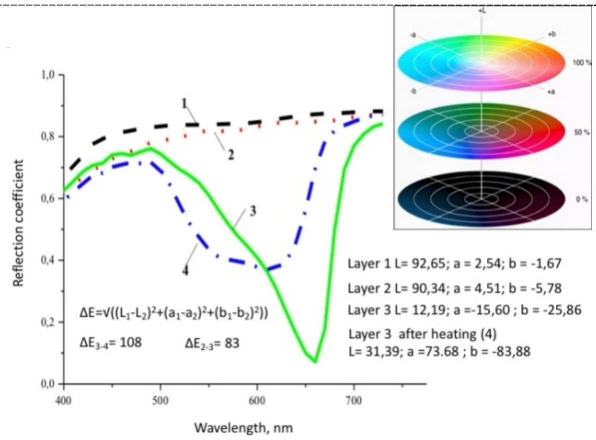

Figure 9. The compatibility instance of the reflection spectrum of normal (curve 3) and defected (curve 4)

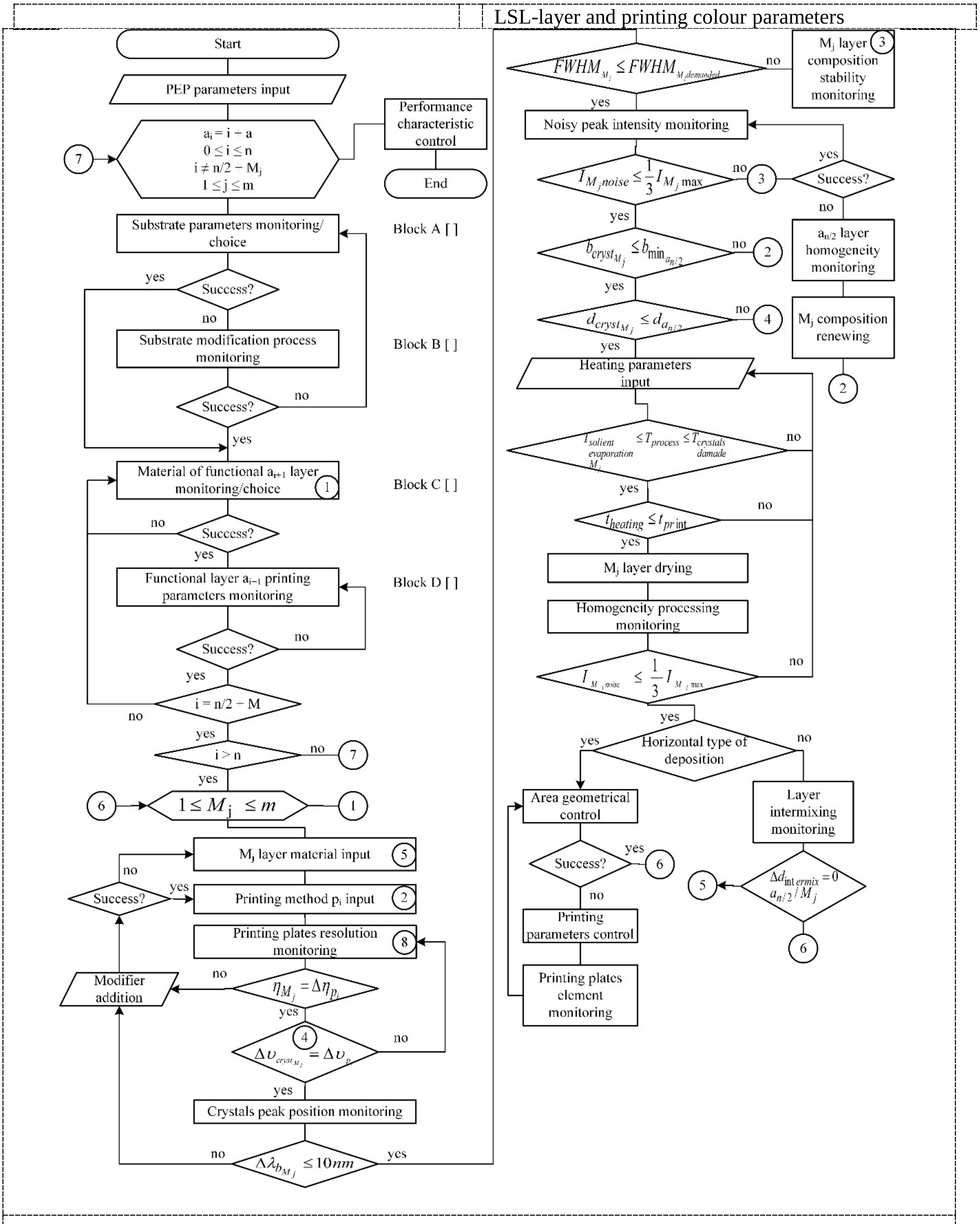

Figure 10. The segment of the printed electronics verification in-process algorithm at the LSL-production stage

As exemplified by PD J-aggregation at the flexographic printing, provided that velocity, temperature and pressure in the engage zone are adjusted, it needs to monitor parameters stability in time, predominantly LSL-inks viscosity and crystallization velocity in the solution as well as the printing plates and the anilox roll geometry. The monitoring procedure should consist of both incoming and permanent verification: initial technical parameters of different printing plates affect to both pixel geometry and matrix spatial resolution (figure 8) [41], at the printing process their geometry is changed due to polymer swelling or impurity at the LSL composition contacting.

These factors incorporation to the LSL quality monitoring is one of the developed algorithm features, which segment at the is LSL production stage is presented in figure 10.

Another algorithm key point is LSL-compounds crystallization velocity monitoring related to the printing speed (figure 10). Such no less important factors of LSL-performance as pixel spreading value control (at the LSL-parallel application scheme), layers intermixing (at the vertical application scheme) monitoring, morphology and relief exam (roughness parameters and layers homogeneity) before and after thermal processing were entered to early presented algorithm segment [37] as well as to the described one. Requirement on optical properties control – additional peaks intensity (figure 9) – after LSL-thermal processing (drying) is driven by the LSL-recrystallization opportunity triggered by either high temperature action or wrong process parameters adjustment.

The technical support feature of the developed monitoring algorithm is the in-process incorporation need for software managed optical controller (a spectrophotometer), which dependable works in a coherent manner at the high printing speed (typically 10-15 thousand A3-format prints per hour).

The modern printing machines are equipped with the automatic colour rendition monitoring systems at the Lab colour space [42] according to standardized parameters – colour coordinates (L, a and b) and colour difference (ΔE) [43], which are the tone value function (printing dots relative area) at the sequential printing inks overlapping.

Referring to figure 9 and [44], these parameters can be effectively used as the direct characteristic of the LSL-structure reorganization driven by any reasons (heating as exemplified). Consequently, the problem of the contactless optical parameters in-process monitoring can be solved by LSL-colour parameters correspondence determination –the calibration curves with tolerances in terms of colour coordinates and colour differencefor each LSL-type. The one of the technique advantages is optical properties monitoring of achromatic functional layers at the operational printing speed. The technique adaptation point is both sensitivity and spatial resolution improvement.

Conclusion

The presented in-process monitoring algorithm of the printed LED pixels production is targeted at the basicsdeveloping of the automated quality control system for novel production area. The algorithm practical relevanceconsists of such production factors considering as printing plates in-process volatility, LSL-crystallization velocity effect and LSL-compounds parameters changeability in time. The contactless technique conception of both LSLand other functional layers optical properties in-process high-speed monitoring based on colour coordinates and colour difference diagnostics is outlined.

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