

# Optical technologies, thin films and interfaces for organic photonics

In the last decades, organic compounds brought a technological revolution in the field of miniaturised light sources and photovoltaic devices. Organic electroluminescent devices have become increasingly important because of their potential applications for large area flat-panel displays and solid-state lighting. The tuneable emission and high fluorescence quantum efficiency make organic materials attractive also for the development of optical amplifiers, lasers and photo-detectors, as well as for photovoltaic devices and solar cells. All these novel organic devices are based on thin-film hetero-structures. In the last years, in the framework of the national research project TECVIM, we have focused on growth methods of organic and nano-structured thin films for organic photonics, spectral investigation of their light-emission properties and degradation mechanisms, laser imaging and patterning technologies, methods of electronic characterisation of interfaces, optical modelling of multilayers, which are critical for the overall improvement of multi-layered device performances

■ Rosa Maria Montereali, Francesca Bonfigli, Dorian Brogioli, Antonino Santoni, Maria Aurora Vincenti, Enrico Nichelatti

## Tecnologie ottiche, film sottili e interfacce per la fotonica organica

Negli ultimi 25 anni, i materiali organici hanno rivoluzionato la tecnologia delle sorgenti di luce miniaturizzate e dei dispositivi fotovoltaici. La rilevanza tecnologica dei dispositivi organici elettroluminescenti è fortemente cresciuta per le loro potenziali applicazioni negli schermi piatti a larga area e nell'illuminazione a stato solido. L'accordabilità dell'emissione luminosa e l'elevata efficienza quantica dei materiali organici li rendono particolarmente promettenti anche per lo sviluppo di amplificatori ottici e laser, fotorivelatori a stato solido, nonché dispositivi fotovoltaici e celle solari. Tutti questi dispositivi organici innovativi sono basati su etero-strutture a multistrato costituite da film sottili. Negli ultimi anni, nell'ambito del Progetto di Ricerca nazionale TECVIM, abbiamo studiato e sviluppato metodi di crescita di film organici e nano-strutturati per la fotonica organica, la caratterizzazione delle proprietà spettrali dell'emissione luminosa e dei suoi meccanismi di degradazione, le tecnologie di imaging e patterning mediante laser, la caratterizzazione elettronica delle interfacce, la modellistica ottica dei multistrati, che sono critici per il miglioramento delle prestazioni dei dispositivi organici

In the last decades, organic compounds brought a technological revolution in the field of miniaturised light sources. In particular, since Tang and Van Slyke

in 1987<sup>[1]</sup> demonstrated efficient electroluminescence (EL) from an organic light-emitting diode (OLED) based on thin film technology, there has been large interest in these materials and devices for flat and flexible full-colour panel displays<sup>[2]</sup> and for low-consumption solid-state illumination.

Organic semiconductors are a broad class of materials that comprises small molecules and conjugated polymers. The relative easiness of handling, the chemical

■ Rosa Maria Montereali, Francesca Bonfigli, Dorian Brogioli, Antonino Santoni, Maria Aurora Vincenti  
ENEA, Technical Unit for Radiation Application Development  
■ Enrico Nichelatti  
ENEA, Technical Unit for Material Technologies

tuning of their emission properties, the low synthesis cost combined with their high fluorescence quantum efficiency, make organic materials attractive for the development of optical amplifiers<sup>[3]</sup>, lasers<sup>[4]</sup> and photo-detectors<sup>[5]</sup>. In recent years, there has been a great deal of interest in organic semiconductors also for photovoltaic (PV) devices, solar cells<sup>[6]</sup>, and field-effect transistors. All these novel organic devices<sup>[1-6]</sup> are based on thin-film hetero-structures. One of their main advantages is that they can be manufactured at low temperatures on flexible substrates by simple fabrication processes like coating, spraying and printing techniques. Moreover, by defining structures at sub-micron level into organic media, *i.e.*, on a spatial scale comparable with their emission wavelengths, the interaction between light and matter can be exploited to engineer novel effects in the emerging field of nano-photonics<sup>[7]</sup>.

In these last years, in the framework of the national research project TECVIM, we have focused on the development of thin-film growth techniques, spectral investigation of their light-emission properties and degradation mechanisms, laser patterning technologies, optical modelling, and electronic characterisation methods of interfaces, which are critical for the improvement of OLED performances. They can be extended to other kinds of functional photonic and electronic devices that are based on organic-dielectric-metallic thin film hetero-structures. An overview of the main results is here reported.

### Growth and optical characterisation of organic thin films and OLED

The most studied low-molecular-weight molecule is a metal-chelate, tris (8-hydroxy-quinoline) aluminium ( $\text{Alq}_3$ ), commonly vacuum deposited as the active layer in green OLEDs in the form of thin film of typical thickness less than 100 nm.

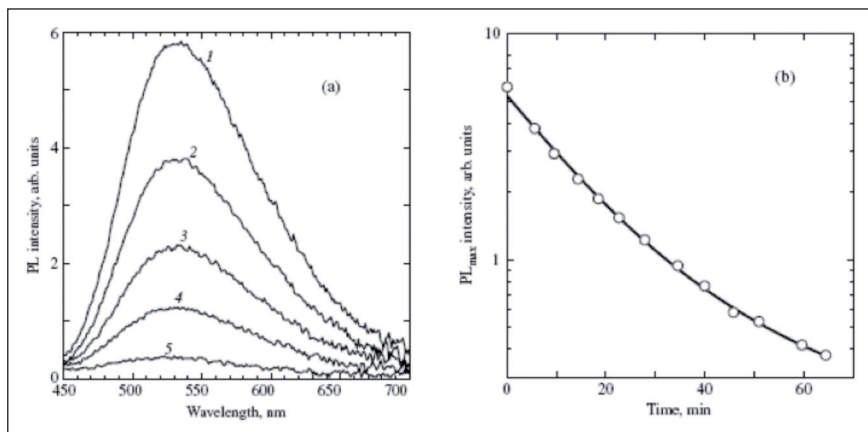
The basic device structure of an OLED consists of one or more organic layers sandwiched between a high-work-function and Transparent Conducting Oxide (TCO) anode, generally Indium Tin Oxide (ITO), and a low-work-function metallic cathode. A small electron injection barrier height at the organic/metal electrode interface is favoured to increase the OLED efficiency.

Al thin films are preferred as cathode due to their better environmental stability and their straightforward use as contact material in Si-based integrated circuits. Insertion of an ultra-thin lithium fluoride (LiF) layer – of typical thickness below 15 nm – between the organic film and the Al cathode was found to significantly reduce the threshold voltage in  $\text{Alq}_3$ -based<sup>[8]</sup> OLEDs. In 2001, for the first time in Italy, a double-layer  $\text{Alq}_3$ -based OLED with a LiF/Al cathode was realised and characterised by our group<sup>[9]</sup> at ENEA Frascati Research Centre. Currently the experimental activities about thermal evaporation of organic ( $\text{Alq}_3$ ), dielectric (LiF) and metallic (Al) thin films<sup>[10]</sup> are finalised to investigate their optical and morphological characteristics and improve growth reproducibility.

### *Photo-degradation of thermally evaporated $\text{Alq}_3$ thin films for organic photonics*

Many efforts have been devoted to increase the lifetime of organic encapsulated devices by studying the effects of several degradation processes, primarily associated with the degradation mechanisms of the electrode materials and electrode/organic interfaces<sup>[11]</sup>. The exposure of transporting molecular layers to ambient factors, like moisture, oxygen and light induces degradation phenomena and the quenching of their green photoluminescence (PL)<sup>[12]</sup>. Thermally evaporated  $\text{Alq}_3$  thin films were used to study the degradation behaviour under thermal treatments in different atmosphere<sup>[13]</sup> by means of optical absorption and photoluminescence linear spectroscopy<sup>[14]</sup>.

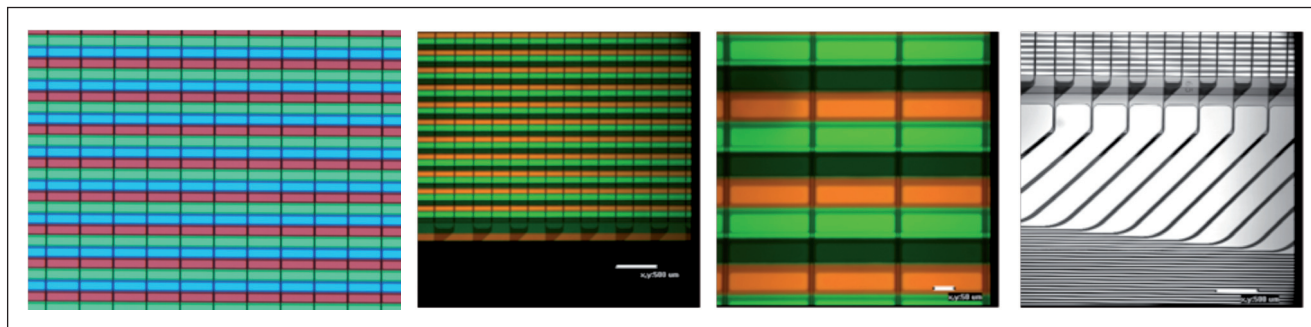
The photo-bleaching effects under selective ultraviolet (UV) and blue light illumination on the photoluminescence spectra of thermally evaporated  $\text{Alq}_3$  thin films were also investigated<sup>[15]</sup>.  $\text{Alq}_3$  thin films of different thicknesses, from 50 to 80 nm, were thermally evaporated onto amorphous glass and fused silica substrates. They were kept in the evaporation chamber under low vacuum pressure ( $10^{-3}$  mbar) in the dark for a few days and, after their first exposure to air and the measurement of their initial optical characteristics, the time evolution of their PL spectra was monitored under selective illumination with UV and blue LEDs. UV light illumination at 385 nm induced a strong and fast decrease in the  $\text{Alq}_3$  films PL intensity. In Figure 1a, seven



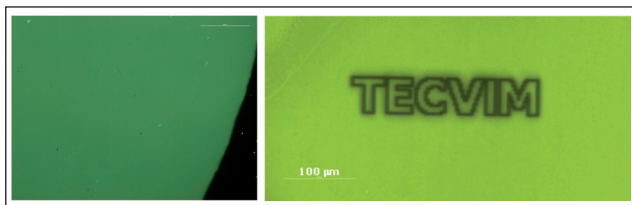
**FIGURE 1** a) PL spectra of an Alq<sub>3</sub> film (50 nm thick) thermally evaporated on a silica substrate, measured at different irradiation times under UV LED illumination: 1-0 min, 2-5 min, 3-15 min, 4-30 min, 5-60 min. b) PL peak intensity at different irradiation times under UV LED illumination. The best fit (solid line) of the experimental points with a double exponential decay curve is reported

ral PL spectra measured at different irradiation times under UV LED illumination were reported. In Figure 1b, the experimental values of the peak intensity of the PL spectra, measured every 5 min, were reported in a logarithmic scale as a function of the irradiation time. The observed behaviour can be described as the sum of two exponential decays, as confirmed by the best fit. We also deduced that the significant reduction in the PL intensity is accompanied by a slight modification of the spectral characteristics of the Alq<sub>3</sub> film broad emission (blue shift). The spectral position of film fluorescence is found to be correlated with both the molecular density of the packing and the length of interligand contacts between neighbouring Alq<sub>3</sub> molecules: the shorter the contacts, *i.e.*, the denser the film, the more the fluorescence is red-shifted.

To explore the role of the energy of the impinging light, similar experiments were performed under illumination of a blue diode, whose emission is peaked at 455 nm, in the spectral range where the optical absorption and emission spectra of Alq<sub>3</sub> films overlap. Again, a decrease in the Alq<sub>3</sub> PL intensity was observed [15]. The photo-bleaching process was less effective as the blue-light spectrum is outside the main absorption band of Alq<sub>3</sub>. Indeed, at the wavelengths of the blue LED that are longer than those of the UV one, spectrally centred around the peak of the Alq<sub>3</sub> main absorption feature, the excitation probability is reduced. The observed behaviour demonstrates that Alq<sub>3</sub> molecules in their excited state are involved in these complex degradation phenomena.



**FIGURE 2** Optical images of a commercial three-color OLED display, 128x128 dots: wide-field conventional fluorescence under UV excitation, a); confocal fluorescence under argon laser excitation at 457.9 nm with two different magnification levels, b,c); confocal in reflection mode under the same laser illumination, d)



**FIGURE 3** Fluorescence image, under blue excitation, of an  $\text{Alq}_3$  film, 50 nm thick, thermally evaporated on a glass substrate at low magnification, a); fluorescence image of a micrometric-sized bleached pattern, the word **TECVIM**, directly written by an argon laser with a confocal microscope, on an  $\text{Alq}_3$  thin film, observed under blue illumination at a higher magnification, b)

### Confocal laser scanning microscopy of organic thin films and OLED

At the ENEA Frascati Research Centre, conventional optical and confocal laser microscopies<sup>[16]</sup> were used to check the quality of light-emitting organic thin films and commercially available OLED displays, as shown in Figure 2.

### Laser writing of micro-patterns in broad-band light-emitting $\text{Alq}_3$ thin films

Photo-bleaching phenomena can also be exploited for direct laser patterning of  $\text{Alq}_3$  thin films with a confocal laser scanning microscope. The photo-bleaching of the green PL signal during light and laser exposures is very effective, depending on the selection of the illumination wavelength and the used power<sup>[15]</sup>. As an example, Figure 3 shows the fluorescence images of thermally evaporated  $\text{Alq}_3$  thin films. In Figure 3b, the intense green fluorescence, visible at naked eye, is

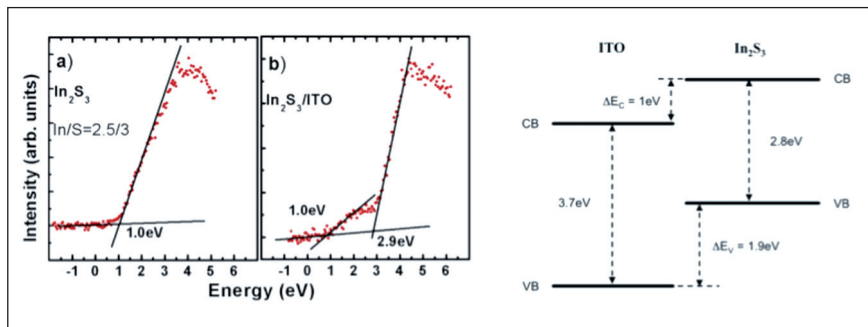
emitted by the organic film with the exception of a dark micrometric pattern that forms to the word **TECVIM**. It was directly written on the  $\text{Alq}_3$  film by an argon laser beam operating at 457.9 nm. The irradiation pattern was controlled by using the galvanometric mirrors of the confocal microscope.

### Growth of nano-structured films and electron spectroscopy of interfaces in hybrid organic-semiconductor cathodes

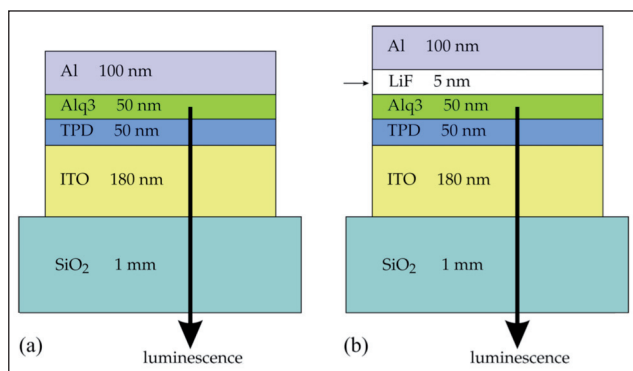
The understanding of the interface properties and the control of the interface formation are crucial for organic device tailoring. Being layered devices, OLED and thin-film solar cells performances are strongly affected by the interface properties as well, and the basic parameters characterising the interface are the band discontinuities at the hetero-junctions between the layers constituting the device stack.

### X-Ray Photoelectron Spectroscopy of PV Device Cathodes

In their common configuration, polymer solar cells have a TCO electrode acting as the high-work function anode for hole collection and a low-work function metallic cathode acting as the electron collector. As a low-work function metal electron collector is air-unstable and highly reactive, an inverted scheme can be used which allows to use a TCO film as the cathode and a low-reactive, non-oxidizing high-work function metal anode<sup>[17]</sup>. The performance of these devices (both in common and in reverse configuration) can be improved by using a semiconductor as



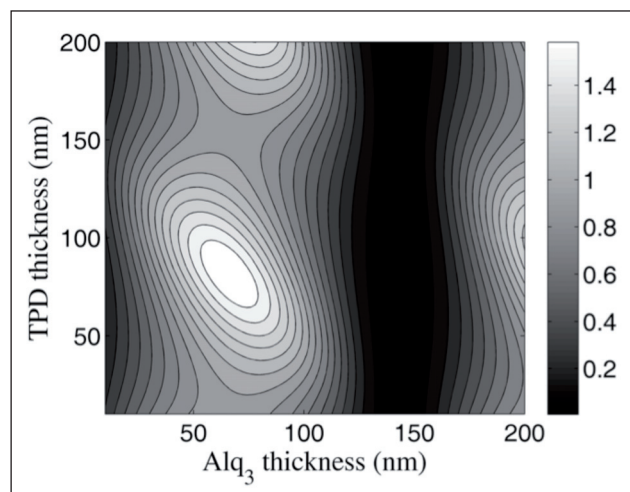
**FIGURE 4** XPS VB spectra of a  $\text{In}_2\text{S}_3$  layer (ratio  $\text{In}/\text{S}=2.5/3$ ). a), VB top measured on the  $\text{In}_2\text{S}_3$  layer; b), Simultaneous detection of the two VB band edges at the  $\text{In}_2\text{S}_3/\text{ITO}$  interface. c), Schematic of the estimated energy level diagram at the  $\text{In}_2\text{S}_3/\text{ITO}$  interface



**FIGURE 5** OLED based on an active Alq<sub>3</sub> layer. Designs containing an Al cathode, a) and a LiF/Al cathode, b)

the electron selective layer<sup>[18]</sup> which is introduced between the active layer and ITO. In<sub>2</sub>S<sub>3</sub> has gained increasing interest in solar cell technology because it has been identified as a suitable alternative to CdS buffer layer in thin-film solar cells. Copper indium gallium (di)selenide (CIGS) cells with In<sub>2</sub>S<sub>3</sub> buffer layers co-evaporated from In and S powder have shown efficiencies of up to 12.4%. In<sub>2</sub>S<sub>3</sub> can be prepared with low-cost techniques such as Chemical Spray Pyrolysis (CSP)<sup>[19]</sup>. We have investigated the band discontinuities at the interface between ITO and an In<sub>2</sub>S<sub>3</sub> layer deposited by CSP by means of X-Ray Photoelectron Spectroscopy (XPS). The band discontinuity at the valence band has been evaluated by a direct method involving the measurement of the valence band at a suitable thickness that allows the simultaneous detection of the band edges of both layers<sup>[20]</sup>, and also by an indirect method requiring the acquisition of the binding energy of selected core levels<sup>[21]</sup>.

As an example, Figs. 4a,b show the valence band (VB) XPS spectra measured on an In<sub>2</sub>S<sub>3</sub>/ITO interface, which depend on the In<sub>2</sub>S<sub>3</sub> layers composition. Figure 4a shows the XPS VB spectrum taken on the bare In<sub>2</sub>S<sub>3</sub> layers and Figure 4b shows the XPS VB data measured on the In<sub>2</sub>S<sub>3</sub>/ITO interface region. The top of the valence band was measured by linear extrapolation of the XPS valence band leading edge. The accuracy of this method has been reported to be usually 0.1 eV or less if the density of states in the valence band re-



**FIGURE 6** Contour map of the theoretical power (a.u.) at  $\lambda = 530$  nm radiated by the OLED of Figure 5b along the normal direction for varying thicknesses of the TPD and Alq<sub>3</sub> layers

gion is known. Data show that on the In<sub>2</sub>S<sub>3</sub> layer (Figure 4a) the VB onset occurs at 1.9 eV above the ITO VB onset (Figure 4b). VB data at the interface show the simultaneous presence of both In<sub>2</sub>S<sub>3</sub>- and ITO-induced valence bands. By taking into account the uncertainties on the VB onset determination ( $\pm 0.1$  eV) the In<sub>2</sub>S<sub>3</sub>/ITO VB offset can be estimated to be  $(1.9 \pm 0.2)$  eV. The VB offset at the In<sub>2</sub>S<sub>3</sub>/ITO interface was also determined by means of the “indirect” method<sup>[21]</sup>. From our experimental XPS data<sup>[22]</sup> and accounting for the error propagation, the indirect VB offset,  $\Delta E_{v_i}$ , results to be  $(1.8 \pm 0.3)$  eV, in good agreement with the direct method result. By knowing the VB offset  $\Delta E_{v_i}$ , also the conduction band offset  $\Delta E_C$  between the conduction bands can be estimated if the gap energies (differences between the conduction, CB, and valence band, VB, energies) are known. By assuming an energy gap of  $(2.8 \pm 0.1)$  eV for In<sub>2</sub>S<sub>3</sub> and  $(3.7 \pm 0.1)$  eV for ITO,  $\Delta E_C$  results in  $(1.0 \pm 0.4)$  eV. In Figure 4c, a sketch of the estimated band diagram is shown.

#### Growth of nano-structured ultra-thin LiF films for OLED cathodes

An analysis of the role and properties of the LiF ultra-thin layer is complicated by its very limited

thickness and its interactions with neighbouring materials<sup>[9,10]</sup>.

Ultra-thin polycrystalline LiF films of controlled nominal thickness below 20 nm were grown by thermal evaporation on several substrates under different conditions; their morphological features were investigated by means of atomic force and scanning electron microscopy and their electronic properties characterised by means of XPS spectra<sup>[23]</sup>. A comparison among ultra-thin LiF films of different thicknesses indicates that the geometric interaction between the arriving ad-molecules and the roughness of the growing surface is the dominant effect in their nanostructuring and the covering of the substrate increases with thickness<sup>[10]</sup>.

### Optical Modelling of an Alq<sub>3</sub>-based Organic Light-Emitting Diode

The internal quantum efficiency of OLED is mainly affected by the non-radiative electron-hole recombination loss<sup>[24]</sup> and singlet-triplet branching ratio. Most of electro-phosphorescent OLED materials have very small non-radiative loss. On the contrary, the external coupling efficiency of a conventional OLED device remains very low. For the purpose of applications such as illumination and flat-panel displays, light emitted from the substrate surface (external modes) in only 20% of the total emitted light from inside the OLED devices<sup>[25]</sup>.

Among the novel approaches implemented to improve the external efficiency<sup>[26]</sup>, designing suitable boundary conditions have been demonstrated to play a key role in the control of spontaneous emission. The theory of light emission from a single point source, such as an atomic (molecular) system, sandwiched between two plane parallel mirrors – either metallic or Bragg reflectors – is well assessed in both its quantum<sup>[27-30]</sup> and classical flavours<sup>[31-34]</sup>. In this context, the classical approach developed by Benisty and co-workers<sup>[34]</sup> relies on the superposition of linearly polarised fields that, after having been generated by suitable elementary dipole source-terms, interact with the surrounding environment. The radiated electromagnetic field and correspon-

dent power are evaluated in a straightforward way by means of analytical formulas<sup>[34]</sup>.

Recently, Benisty's theory has been expanded into a more general theory to deal with a collection of point sources so densely packed – with respect to the involved wavelengths – to be viewed as a continuous active volume<sup>[35-36]</sup>. Still maintaining its analyticity, this generalised theory includes even the cases of partial and total cooperation among the volume elements in the emission process<sup>[37]</sup>. The case of an Alq<sub>3</sub>-based multilayer OLED can be dealt with in this theoretical framework. For simplicity, distinct elements of the Alq<sub>3</sub> layer are assumed not to cooperate in the emission process, so that the power that is radiated by the device can be simply viewed as the integral of elementary contributions  $w(\mathbf{r})$  coming from single dipoles located at each point  $\mathbf{r}$  of the Alq<sub>3</sub> layer<sup>[35-36]</sup>. The integration is straightforward once the expression of  $w(\mathbf{r})$  is taken into account<sup>[35-36]</sup>. By using the resulting analytical formulas<sup>[36]</sup>, one can theoretically predict the angular and spectral distributions of the radiated power and its total amount; also, an estimation of how the device efficiency depends on various features of the multilayer is feasible.

Two Alq<sub>3</sub>-based OLED configurations, shown in Figure 5, are taken into account. In one of them, see Figure 5b, an ultrathin (5 nm) layer of LiF is placed in contact with the Al cathode to lower the threshold voltage of the device<sup>[38]</sup>. In the following, a 10-nm-thin radiating portion of the Alq<sub>3</sub> layer on the TPD side is assumed<sup>[36]</sup>. Our goal is to check how the LiF layer influences the device not only electrically, but also optically – despite its ultra-thin thickness. The answer is found through the generalised theory: such a thin layer of LiF is able to increase the electroluminescence emerging from the device at, e.g.,  $\lambda = 530$  nm by 11% (full solid-angle integration)<sup>[36]</sup>. One could also wonder whether the design thickness values of the considered OLED are optimal or if they could be suitably changed to improve the overall *optical* efficiency. Such a parametric study can be performed quite effortlessly thanks to the analytical formulas of the generalised theory. Figure 6 displays a contour map of the theoretical power

that emerges from the device of Figure 5b along the normal direction vs. the thicknesses of the Alq<sub>3</sub> and TPD layers. One can notice that the maximum of power corresponds to a thickness of ~70-80 nm for both the Alq<sub>3</sub> and TPD layers instead of the design's one (50 nm). For such thickness values, the device improves its optical efficiency by about 60-65%, at least along the normal direction<sup>[36]</sup>.

## Conclusions

Thin films of Alq<sub>3</sub>, commonly vacuum deposited as the active layer in green OLEDs, were grown by thermal evaporation under controlled conditions and their optical absorption and emission properties were used to study the degradation behaviour under ambient atmosphere and/or light exposure in order to increase their lifetimes.

Conventional optical and confocal laser microscopies were successfully used to check the quality of light-emitting organic thin films and commercially available three-color OLED displays. The photobleaching phenomena were also exploited for direct laser patterning of the investigated Alq<sub>3</sub> thin films at micrometric scale with a confocal laser scanning microscope.

Being layered electroluminescent devices, OLED and thin-film solar cells performances are strongly affected by the interface properties. X-ray photoelectron spectroscopy was used to investigate some

basic parameters that characterise the interface and the band energy discontinuities at the heterojunctions between the layers constituting the device stack. In electro-luminescent OLED, the insertion of an ultra-thin LiF layer between the organic film and the metallic Al cathode was found to significantly reduce the threshold voltage in Alq<sub>3</sub>-based OLEDs. Nano-structured polycrystalline LiF films, grown by thermal evaporation on different substrates, were investigated. In polymer solar cells, which feature a TCO electrode acting as the high-work function anode for hole collection, the efficiency can be improved by using a semiconductor, In<sub>2</sub>S<sub>3</sub>, as the electron selective layer which is introduced between the active layer and ITO. Their valence band diagram was evaluated.

Finally, an analytical model which describes the effect of optical confinement in a multilayer on light emission from a hybrid organic-dielectric-metal structure was enhanced and successfully applied to a conventional basic OLED device to explain the increase in the external coupling efficiency with the introduction of an ultra-thin LiF layer below the Al cathode.

The above-discussed technologies are suitable for the realisation and characterisation of functionalised optical and electronic thin-film devices of higher efficiencies and open interesting perspectives in the fast-growing field of organic photonics and its application to alternative energy and sustainable development. ●

### Acknowledgments

The authors are indebted to S. Almaviva, G. Baldacchini, L. Caneve, A. Mancini, M.R. Rajesh Menon, and A. Rufoloni for fruitful discussions. Useful suggestions given by R. Fantoni are also acknowledged. Many thanks are due to L. Cantarini, R. Giovagnoli, S. Libera for their skilful support. Research carried out within TECVIM (TECnologie per la Visualizzazione di Immagine) project, funded by MIUR, the Italian Ministry of Education, University and Scientific Research, and with the support of the ICTP Programme for Training and Research in Italian Laboratories, Trieste, Italy.

- [1] C.W. Tang and S.A. VanSlyke, "Organic electroluminescent diodes," Appl. Phys. Lett. 51 (12), 913 (1987).
- [2] J.R. Sheats, H. Antoniadis, M. Hueschen, W. Leonard, J. Miller, R. Moon, D. Roitman and A. Stocking, "Organic Electroluminescent Devices", Science 273, 884 (1996).
- [3] V.G. Kozlov, V. Bulovic, P.E. Burrows, and S.R. Forrest, "Laser action in organic semiconductor waveguide and double-heterostructure devices," Nature 389, 362 (1997).
- [4] I.D.W. Samuel and G.A. Turnbull, "Organic semiconductors lasers," Chem. Rev. 107, 1272 (2007).
- [5] C.H. Lally, G.J. Davies, W.G. Jones, N.J.T. Smith, "UV quantum efficiencies of organic fluors", Nucl. Instr. and Meth. B 117, 421 (1996).
- [6] S. Günes, N.S. Sariciftci, "Hybrid solar cells", Inorganica Chimica Acta 361, 581 (2008)
- [7] F. Antolini, A. Ghezlbash, C. Esposito, E. Trave, L. Tapfer, B.A. Korgel, "Laser-induced nanocomposite formation for printed nanoelectronics," Mat. Lett. 60, 1095 (2006).
- [8] L.S. Hung, C.W. Tang, and M.G. Mason, Appl. Phys. Lett. 77, 3096 (2000).
- [9] R.M. Montereali, S. Gambino, S. Loreti, S. Gagliardi, A. Pace, G. Baldacchini, F. Michelotti, "Morphological, electrical and optical properties of organic light-emitting diodes with a LiF/Al cathode and an Al-hydroxyquinoline/diamine junction," Synthetic Metals 143, 171 (2004).
- [10] M.A. Vincenti, F. Bonfigli, R.M. Montereali, A. Rufoloni, F. Basoli, E. Di Bartolomeo, S. Licoccia, E. Nichelatti, "Crescita e caratterizzazione di film sottili per diodi organici emettitori di luce," ENEA Technical Report RT/2011/19/ENEA, ISSN/0393-3016 (2011).
- [11] H. Aziz, Z.D. Popovic, N.X.Hu, A.M. Hor, G. Xu, "Degradation mechanism of small molecule-based organic light-emitting devices," Science 283, 1900 (1999).
- [12] P. Chiacchieretta, G. Baldacchini, T. Baldacchini, F. Bonfigli, R.B. Pöde, R.M. Montereali, M.A. Vincenti, Proc. Convegno congiunto DGaO/SIOF, Facoltà di Ingegneria Università degli Studi di Brescia, Brescia 2-5 giugno 2009, <http://www.dgao-proceedings.de>, ISSN: 1614-8436.
- [13] G. Baldacchini, S. Gagliardi, S. Gambino, S. Loreti, R.M. Montereali, A. Pace, *Diodi Organici Luminescenti*, Energia, Ambiente e Innovazione 4, 83 (2003).
- [14] G. Baldacchini, S. Gagliardi, R.M. Montereali, A.Pace and R.B. Pöde, "Optical spectroscopy of tris(8-hydroxyquinoline)aluminium thin films," Phyl. Mag. B 82(6), 669 (2002).
- [15] F. Bonfigli, D. Brogioli, M.A. Vincenti, and R.M. Montereali, "Optical investigation of photo-bleaching effects in organic Alq3 thin films," J. Opt. Tech. 78(7),419 (2011).
- [16] F. Bonfigli, M.A. Vincenti, R.M. Montereali, L. Caneve, S. Almaviva, "Caratterizzazione di film sottili di Alq3 e LiF mediante misure LIBS e microscopia ottica," ENEA Technical Report RT/2011/20/ENEA, ISSN/0393-3016 (2011).
- [17] M.S. White, D.C. Olson, S.E. Shaheen, N. Kopidakis, D.S. Ginley, "Inverted bulk-heterojunction organic photovoltaic device using a solution-derived ZnO underlayer", Appl. Phys. Lett. 89, 143517 (2006).
- [18] M. Lira-Cantu, F.C. Krebs, "Hybrid solar cells based on MEH-PPV and thin film semiconductor oxides (TiO2, Nb2O5, ZnO, CeO2 and CeO2-TiO2): performance improvement during long-time irradiation", Sol. Energy Mater. Sol. Cells 90, 2076 (1985).
- [19] Teny Theresa John, S. Bini, Y. Kashiwaba, T. Abe, Y. Yasuhiro, C. Sudha Kartha, K.P. Vijayakumar, "Characterization of spray pyrolysed indium sulfide thin films", Semicond. Sci. Technol. 18, 491 (2003).
- [20] A.D. Katnani, G. Margaritondo, "Microscopic study of semiconductor heterojunctions: photoemission measurements of the valence-band discontinuity and of the potential barriers", Phys. Rev. B28, 1944 (1983).
- [21] J.R. Waldrop, R.W. Grant, S.P. Kowalczyk, E.A. Kraut, "Measurement of semiconductor heterojunction band discontinuities by x-ray photoemission spectroscopy", J. Vac. Sci. Technol. A3, 835 (1985).
- [22] M.R. Rajesh Menon, A. Mancini, C. Sudha Kartha, K. P. Vijayakumar, A. Santoni, "Band offset of the In2S3/Indium Tin Oxide interface measured by X-ray photoelectron spectroscopy", in press on Thin Solid Films, DOI:10.1016/j.tsf.2012.05.012.
- [23] R.M. Montereali, F. Bonfigli, J. Lancok, A. Mancini, V. Mussi, A. Pace, A. Santoni, M.A. Vincenti, Proc. 14th International Workshop on Inorganic and Organic Electroluminescence & 2008 International Conference on the Science and Technology of Emissive Displays and Lighting, Bagni di Tivoli, Rome, Italy, 9-12 September 2008, eds. G. Baldacchini, R.M. Montereali, M.A. Vincenti (2008) ISBN 88-8286-194-5, p.291.
- [24] R. Miscioscia, P. Vacca, G. Nenna, T. Fasolino, V. la Ferrara, P. Tassini, C. Minarini, D. della Sala, "Electrooptical analysis of effects induced by floating metallic interlayers in organic LEDs," IEEE Trans. Electr. Devices 56(9), 1912 (2009).
- [25] K. Saxena, V.K. Jain, D.S. Mehta, "A review on the light extraction techniques in organic electroluminescent devices," Opt. Materials 32, 221 (2009).
- [26] P. Perlo, P.M. Repetto, S. Sinesi, V. Lambertini, D. Pullini, G. Innocenti, "Diffraction and micro-optics at CRF: developed applications for the transport industry", Proceedings of the AMAA Conference, 2000.
- [27] P.W. Milonni and P.L. Knight, "Spontaneous emission between mirrors," Opt. Commun. 9, 119 (1973).
- [28] F. De Martini, M. Marrocco, P. Mataloni, L. Crescentini, and R. Loudon, "Spontaneous emission in the optical microscopic cavity," Phys. Rev. A. 43, 2480 (1991).
- [29] G. Björk, S. Machida, Y. Yamamoto, and K. Igeta, "Modification of spontaneous emission rate in planar dielectric microcavity structures," Phys. Rev. A. 44, 669 (1991).
- [30] P. Meystre and M.I. Sargent, Elements of Quantum Optics, 4th ed. (Springer, Berlin, 2007).
- [31] H. Kuhn, "Classical aspects of energy transfer in molecular systems," J. Chem. Phys. 53, 101 (1970).
- [32] H. Rigneault and S. Monneret, "Modal analysis of spontaneous emission in a planar microcavity," Phys. Rev. A. 54, 2356 (1996).
- [33] S. Ciancaleoni, P. Mataloni, O. Jedrkiewicz, and F. De Martini, "Angular distribution of the spontaneous emission in a planar dielectric dye microcavity," J. Opt. Soc. Am. B. 14, 1556 (1997).
- [34] H. Benisty, R. Stanley, and M. Mayer, "Method of source terms for dipole emission modification in modes of arbitrary planar structures," J. Opt. Soc. Am. A. 15, 1192 (1998).
- [35] E. Nichelatti, "Cooperative spontaneous emission from volume sources in layered media," ENEA Tech. Rep. RT/2009/4/FIM (2009).
- [36] E. Nichelatti, F. Bonfigli, M.A. Vincenti, and R.M. Montereali, "Optical modelling of an Alq3-based organic light-emitting diode," J. Opt. Tech. 78(7), 424 (2011).
- [37] E. Nichelatti, M. Marrocco, and R. M. Montereali, "Cooperative optical effects in volumes embedded in layered media," J. Raman Spectrosc. 41, 859 (2010).
- [38] T.M. Brown, R.H. Friend, I.S. Millard, D.J. Lacey, J.H. Burroughes, and F. Cacialli, "LiF/Al cathodes and the effect of LiF thickness on the device characteristics and built-in potential of polymer light-emitting diodes," Appl. Phys. Lett. 77, 3096 (2000).