

## Optical properties of Inq<sub>3</sub> thin film used in organic light emitting devices

Vivek Kumar Shukla\* and Satyendra Kumar

Department of Physics and Samtel Centre for Display Technologies,  
Indian Institute of Technology Kanpur, Kanpur -208016, India  
\*vkshukla@iitk.ac.in

**Abstract:** In this report, the optical properties of tris-(8-hydroxyquinoline) metal complex Inq<sub>3</sub>; used as light-emitting layer in electroluminescent (EL) devices are shown. The material has been synthesized and the thin films have been deposited by thermal evaporation on quartz and silicon substrates. The optical constants (*n* and *k*) of Inq<sub>3</sub> thin films have been determined using spectroscopic ellipsometry. The other optical properties have been studied using photoluminescence and UV-Visible transmission measurements.

**Keywords:** Tris-(8-hydroxyquinoline) metal complex; Inq<sub>3</sub>; Spectroscopic Ellipsometry (SE); Room temperature (RT).

### Introduction

The first report on tris-(8-hydroxyquinoline) aluminium (Alq<sub>3</sub>) used in electroluminescent device [1] has developed a great deal of interest in the study of its optical properties. Presently, Alq<sub>3</sub> is one of the widely used light-emitting layers in organic light emitting devices (OLEDs). However, instability is a major problem with these devices. The long-term degradation in the devices has been explained due to formation of black spots by moisture and oxygen. Hence, light, air and moisture are very important parameters which affect the properties of the material.

In order to improve the stability of the organic devices, it is required to explore novel organic emitting materials because the optical properties of light emitting materials directly affect the brightness, efficiency and thus the stability of devices. In this direction, different 8-hydroxyquinoline metal derivatives, used as emitting material have been already developed [2,3]. A series of tris-(8-hydroxyquinoline)metal chelates with central atoms like Al, Ga and In have been used for fabrication of OLEDs [4].

Here, we report on the synthesis and thin film formation of tris-(8-hydroxyquinoline) metal complex (Inq<sub>3</sub>), used as light-emitting material in OLEDs, examine the optical properties of the thin films of this material and the effect of light & environment on it. The emission wavelength of this material corresponds to greenish-yellow (~535 nm) color.

### Experimental details

In the process of synthesis of 8-hydroxyquinoline metal complex Inq<sub>3</sub>; 8-hydroxyquinoline was dissolved in CH<sub>3</sub>COOH and this solution was added slowly to InCl<sub>3</sub> solution while stirring. The pH of mixed solution was adjusted using CH<sub>3</sub>COONH<sub>4</sub> to get a maximum yield.

The obtained yellow precipitate was filtered and washed with warm water for several times. The final precipitate was dried. This yellow solid was determined by <sup>1</sup>H NMR, FTIR and elemental analysis to be Inq<sub>3</sub>. The synthesized material was purified using vacuum sublimation method.

Inq<sub>3</sub> films were deposited by thermal evaporation on Si and quartz substrates in a homemade stainless steel chamber in vacuum. Prior to deposition, the substrates were cleaned in an ultrasonic bath followed by different steps with acetone, trichloroethylene, distilled water and ethanol. The Si substrate was also dipped in 5% HF solution for few seconds to remove oxide layer. A molybdenum boat was used for evaporation and substrates were kept at the top of the chamber at room temperature. Thickness of the film during the growth was monitored using HINDHIVAC digital thickness monitor. The thicknesses of the films were also directly measured outside the chamber using Alphastep profiler and also by fitting the data by SE measurements. The thicknesses in all the cases are in good agreement with each other. To compare the optical constants of Inq<sub>3</sub> with Alq<sub>3</sub>, 150 nm thick thin films of both the molecules were deposited on Si substrate, keeping all deposition conditions similar, for spectroscopic ellipsometry (SE) measurements. Alq<sub>3</sub> used for comparison was synthesized and purified in the lab.

Photoluminescence data at room temperature was recorded using a spectrofluorometer (Fluorolog 3, Jobin Yvon) with front face detecting geometry, in which the emitted signal is collected at ~22° with respect to the normal at the surface of the sample, coincident with the excitation light direction. Transmission spectra at room temperature have been measured using Perkin Elmer UV/VIS Lambda 40 Spectrometer in Inq<sub>3</sub> films on quartz substrate.

Spectroscopic ellipsometry (SE) data were recorded on the samples using a phase modulated spectroscopic ellipsometer (UVISEL, Jobin Yvon Horiba) with a wavelength range from 260 to 1700 nm. The incidence angle was 70° and the data were recorded at 0.05 eV intervals in energy scanning modes. In case of phase modulated ellipsometry the measured signal is given by  $I(\lambda, t) = I_o \{1 + I_s \sin \delta(t) + I_c \cos \delta(t)\}$  where  $I_s = \sin 2\psi \sin \Delta$ , and  $I_c = \sin 2\psi \cos \Delta$  allow determination of the ellipsometric angles ( $\psi, \Delta$ ) in the configuration of our measurement set-up [5].

In the present work, we used the modified Forouhi-Bloomer dispersion relations suitable for an amorphous material [6].

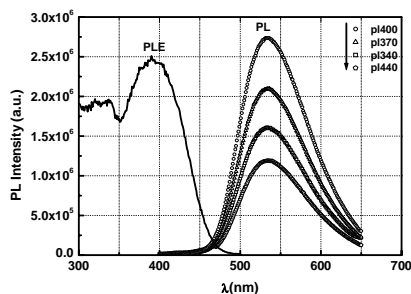
It has been found that two amorphous oscillators ( $j=2$ ) are needed and are sufficient to reproduce the experimental data in the measured spectral range of 260-1700 nm. SE data was analyzed using standard multilayer model. It has been found that two amorphous oscillators are needed and are sufficient to reproduce the experimental data in the measured spectral range [6,7]. Earlier SE data analysis has used the model of Forouhi and Bloomer [8,9] or a combination of conventional [10] or modified Lorentz oscillators [10,11].

AFM measurements were conducted using Molecular Imaging, USA make AFM equipment in non-contact, acoustic AC (AAC) mode. An advantage of AAC mode is that besides the topography image phase image is also obtained. Phase imaging is an added feature of AAC mode AFM which gives the estimation of presence of other phases. In phase imaging AFM, cantilever interaction with sample surface is mapped by measuring change in phase angle between approach and retraction. For stress free surfaces, phase contrast is due to change in chemical composition or due to change in structure.

Thin film samples were exposed to white light using a 50 watt quartz tungsten halogen (QTH) lamp (with a spectral range of 450 to 850 nm), from a distance of 5.5 cm for few hrs at room temperature. One set of samples was exposed in air ambient while other set was exposed in vacuum.

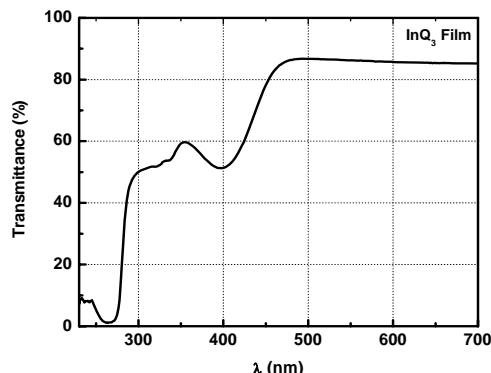
### Results and discussion

Fig.1 shows the room temperature photoluminescence (PL) data on a 650Å thick Inq<sub>3</sub> film deposited at room temperature on quartz substrate. The PL is excited by different wavelengths as indicated in the figure caption. PL peak is observed at ~535 nm for all excitation wavelengths. Photoluminescence excitation (PLE) spectrum is also shown in the figure. PLE is measured at 540 nm wavelength and clearly shows absorption at ~390 nm. The wavelengths near 390 nm look like to contribute mainly in the emission.



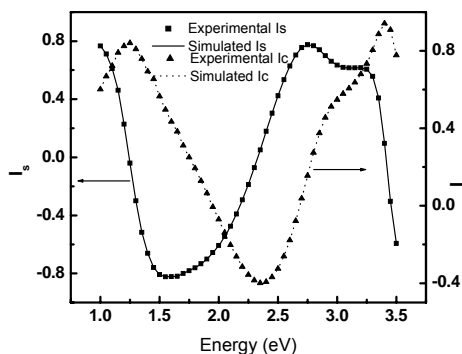
**Figure 1.** Photoluminescence measured on a ~ 650Å thick Inq<sub>3</sub> film. PL is collected at different excited wavelengths (340, 370, 400, and 440 nm). PL excitation spectrum measured at the peak wavelength of 540 nm, is also shown.

UV-VIS transmission spectra of a 2000Å thick Inq<sub>3</sub> film deposited on quartz substrate at room temperature shows main absorption bands peaked at ~ 272 & ~ 390 nm and also some structures in between (Fig.2).



**Fig.2.** Transmittance of a 2000Å thick Inq<sub>3</sub> film deposited on quartz substrate

Fig. 3 shows the measured as well as fitted SE data ( $I_s$  and  $I_c$ ) on Inq<sub>3</sub> film on *c*-Si (Sample A). The measured data are shown as symbols and theoretically fitted data using the three phase (film/SiO<sub>2</sub>/*c*-Si) model with dispersion relations given above are shown as lines. An excellent fit is obtained in the whole spectral range.

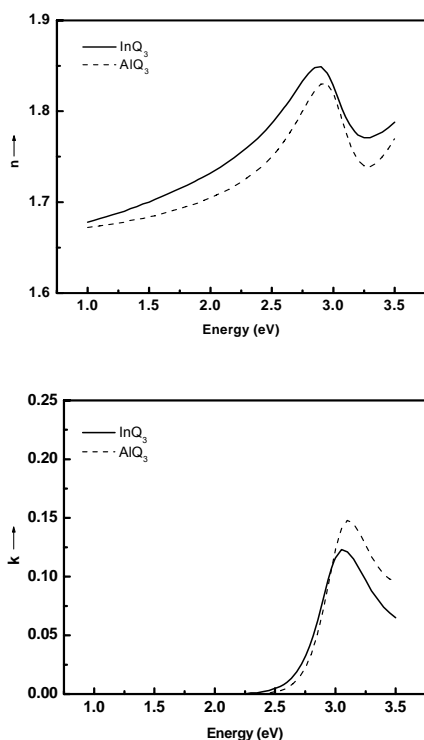


**Fig.3** Measured as well as fitted SE data ( $I_s$  and  $I_c$ ) on Inq<sub>3</sub> film on *c*-Si are shown. The measured data are shown as filled circles ( $I_s$ ) and triangles ( $I_c$ ) and theoretically calculated data using are shown as solid and dotted lines respectively.

The values of dispersion parameters are shown in Table 1. In the table, L is organic layer thickness. In modeling, the thickness of SiO<sub>2</sub> layers is too small to influence the values of optical constants and therefore is neglected. Film thickness obtained from Ellipsometry fit was in excellent agreement with the profilometer measurements.

**Table1:** Model parameters obtained for as deposited and white light exposed in air Inq<sub>3</sub> film deposited on Si substrate.

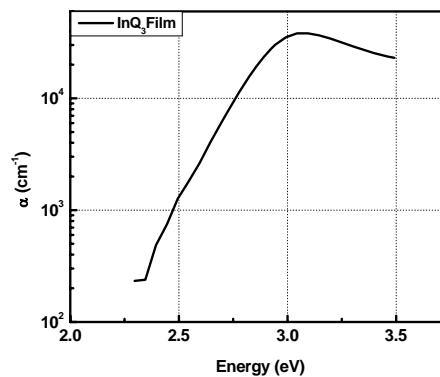
Parameters	As deposited (Sample A)	Light exposed in air for 24hrs
L (A°)	1778.6 ± 6.6	1740.8 ± 7.6
n <sub>∞</sub>	1.492 ± 0.024	1.278 ± 0.090
ω <sub>g</sub> (eV)	2.136 ± 0.099	2.350 ± 0.063
f <sub>1</sub>	0.044 ± 0.008	0.042 ± 0.011
ω <sub>1</sub> (eV)	6.316 ± 0.441	10.656 ± 1.682
Γ <sub>1</sub> (eV)	0.834 ± 0.158	0.760 ± 0.195
f <sub>2</sub>	0.010 ± 0.002	0.017 ± 0.003
ω <sub>2</sub> (eV)	2.988 ± 0.015	2.965 ± 0.017
Γ <sub>2</sub> (eV)	0.254 ± 0.010	0.267 ± 0.014



**Fig.4(a) and 4 (b)** The real (*n*) and imaginary (*k*) parts of the complex refractive index of 150 nm thick Inq<sub>3</sub> (solid line) and Alq<sub>3</sub> (dashed line) films on Si substrate, obtained from dispersion relations fitted to the SE data.

The real (*n*) and imaginary (*k*) parts of the complex refractive index for the Inq<sub>3</sub> film, obtained from the dispersion relation fitted to the SE data are plotted in Fig. 4(a) & (b) and comparison was made with Alq<sub>3</sub> film of nearly same thickness. The nature of a metal ion influences the emission color, efficiency, stability and evaporability of the metal complex. In the structure of these two luminescent materials attached metals are of same group in periodic table which causes the similarity in these two materials. The difference between Alq<sub>3</sub> and Inq<sub>3</sub> can be understood by heavy atom effect. The fluorescence is reduced with increase in atomic number of metal ion caused by increase in intersystem crossing. Also, as the covalent nature of metal-ligand bonding is increased, the emission shifts to longer wavelength. For example, the chelate formed with In is more shifted towards longer wavelength than formed with Al.

The value of reflection coefficient (*n*) for Inq<sub>3</sub> film is slightly higher in full spectral range while the value of extinction coefficient (*k*) is lower above 2.8 eV. The value of reflection coefficient shows higher packing density of Inq<sub>3</sub> film which is one of the useful parameter in the stability of devices. The value of absorption coefficient in the full spectral range is calculated from the value of *k* (Fig.5). The absorption shows a peak near 3.05 eV. Using the Forouhi-Bloomer dispersion relations on our amorphous Inq<sub>3</sub> thin films also leads to a reduction in the total number of fitting parameters as compared to the modified Lorentz oscillators [10, 11, 12].



**Fig.5** The absorption coefficient calculated from imaginary (*k*) parts of the complex refractive index of Inq<sub>3</sub> film obtained from dispersion relations fitted to the SE data.

### Conclusion

The organic light emitting material Inq<sub>3</sub> has been synthesized in the lab. Transmission and PLE spectrum of thin films of this material shows that most of the absorption is at 390 nm while PL peaks around 535 nm which shows the nonradiative transition in this material. The optical functions (*n* and *k*) have been determined using spectroscopy ellipsometry and compared with that of Alq<sub>3</sub> in an extended wavelength range.

### Acknowledgements

We acknowledge financial support from the Department of Science and Technology, New Delhi and Samtel Group of Industries.

### References

1. C. W. Tang and S.A. VanSlyke, *Appl. Phys. Lett.* 51 (1987) 913.
2. Yuji Hamada, Takeshi Sano, Masayuki Fujita, Takanori Fujii, Yoshitaka Nishio, Kenichi Shibata, *Jpn. J. Appl. Phys.* 32(1993) L 514.
3. Linjun Wang, Xueying Jiang, Zhilin Zhang, Shaohong Xu, *Displays* 21 (2000) 47.
4. Baijun Chen, Xiaoqin Lin, Laifung Cheng, Chun-Sing Lee, William A Gambling and Shuit-tong Lee, *J. Phys. D: Appl. Phys.* 34 (2001) 30.
5. B. Drevillon, *Prog. Crystal Growth Charact.* 27 (1993)1.
6. Satyendra Kumar, Vivek Kumar Shukla, Ashutosh Tripathi, *Thin Solid Films*, 477 (2005) 240.
7. Satyendra Kumar, A.K. Biswas, V.K. Shukla, A. Awasthi, R.S. Anand, J. Narain, *Synthetic Metals* 139 (2003) 751.
8. B. Masenelli, A. Gagnaire, L. Berthelot, J. Tardy, and J. Joseph, *J. Appl. Phys.* 85 (1999) 3032.
9. A.R. Forouhi, and I. Bloomer, In: E.D. Palik (Ed.), *Handbook of Optical Constants of Solids II*, Academic Press, San Diego, 1991, p. 151.
10. W. Xie, Y. Zhao, J. Hou and S. Liu, *Jpn. J. Appl. Phys.* I, 42 (2003) 1466.
11. A.B. Djuricic, C.Y. Kwong, W.L. Guo, T.W. Lau, E.H. Li, H.S. Kwok, L.S.M. Lam and W.K. Chan, *Thin Solid Films* 416 (2002) 233.
12. A.B. Djuricic, C.Y. Kwong, T.W. Lau, E.H. Li, Z.T. Liu, H.S. Kwok, L.S.M. Lam and W.K. Chan, *Appl. Phys. A* 76 (2003) 219.