Optical properties of Electroluminescent Zinc(IIbis(8-hydroxyquinoline) thin films prepared at different deposition rates

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Abstract: *Structural and optical properties of Zinc(II) bis(8-hydroxyquinoline) (ZnQ_2) were studied as a function of deposition parameters. Optical functions were determined by modeling the spectroscopic ellipsometric data using two different dispersion relations in the energy range 1.5eV-4.5eV. Structural changes were quantified with aid of atomic force spectroscopy. By using accurate thickness of the film found from the transparent region, major bands in the optical absorption region are revealed. Radiative behaviors of these bands were studied using the photoluminescence excitation and absorption data .Optical functions were found to vary considerably as the structure of the films changed with deposition rate.*

Keywords: ZnQ_2; Ellipsometry; Deposition Rate.

Introduction

Organic luminescent materials have been studied in past for their optical properties. Studies on thin films of polymer and small molecule based luminescent materials have been the key to understand their basic molecular interaction and their luminescence. Many Small molecules such as metal based Quinoline derivatives have shown promising results as strong contenders for future display technology. [1-5] Extensive work has been done on tris-(8-hydroxyquinoline) aluminum (AlQ_3) due to its properties such as excellent flexibility, high photoconductivity, and high life time of devices. However, properties of other metal based quinoline derivatives still need to be explored as well. ZnQ_2 has shown advantages over AlQ_3 in electron transport and shown higher quantum yields in device performance which results in lower operating voltages[7].

Small molecule thin films are typically deposited by thermal vacuum sublimation techniques [6]. Though several deposition techniques have been attempted [7,8,9], thermal vacuum sublimation is still preferred method as it has advantages of giving high quality thin films which yield high life-time devices.

Optical properties of thin film organic luminescent materials are direct consequence of intermolecular interactions, resulting from π-π stacking [5, 8, 9]. Thin film effects that affect optical dielectric function can be studied using sensitive optical instruments like Spectroscopic Ellipsometry.

In this article we study the effect of deposition rates on structural and optical properties of ZnQ_2. Fabrication and characterization techniques are described in the next section followed by results and discussion.

Experimental Details

Sample Preparation: As different types substrates were needed for various experiments, a variety of suitable methods were used for cleaning. The substrates were properly washed for organic removal and then cleaned using a solution 5:1:1 solution of DI water, Hydrogen Peroxide and Ammonia at a temperature of 80°C for 20 min. The substrates were thoroughly rinsed before and after the cleaning procedure. The cleaned substrates were dried and then dipped into solution of 5ml HF and 95 ml Methanol for 2 minutes for the removal of the native oxide on the Si substrates.

The substrates were mounted in our ultra high vacuum thermal sublimation machine which has a base pressure of ~10^{-8} mbar using a load lock system. The deposition rate was controlled by precise change of crucible temperature. Average film thickness was kept 100 nm. The exact pressure, crucible temperature during depositions and other details are mentioned in Table1.

Table1.Experimental details and AFM Roughness (RMS) for the ZnQ_2 on Si substrates.

Sample Name	T (^{o}C)	P ($\times 10^{-7}$mbar)	Deposition Rate(A/s)	RMS Roughness $(500nm)^2$	RMS Roughness $(10,000)^2$
z0p2	290 ± 2	3.9	0.2 ± 0.1	21.1 ± 6.2	56.9 ± 6.6
z0p5	310 ± 3	6.4	0.5 ± 0.1	57.9 ± 10.2	100.4 ± 1.8
z1p0	312 ± 2	8.4	1.0 ± 0.1	17.1 ± 6.2	76.9 ± 11.0
z1p5	316 ± 2	15.0	1.5 ± 0.2	68.1 ± 8.6	107.5 ± 12.2
z2p0	320 ± 2	13.0	2.0 ± 0.2	49.2 ± 9.5	84.5 ± 4.1
z2p5	327 ± 4	16.0	2.5 ± 0.3	67.4 ± 20.4	107.6 ± 6.7

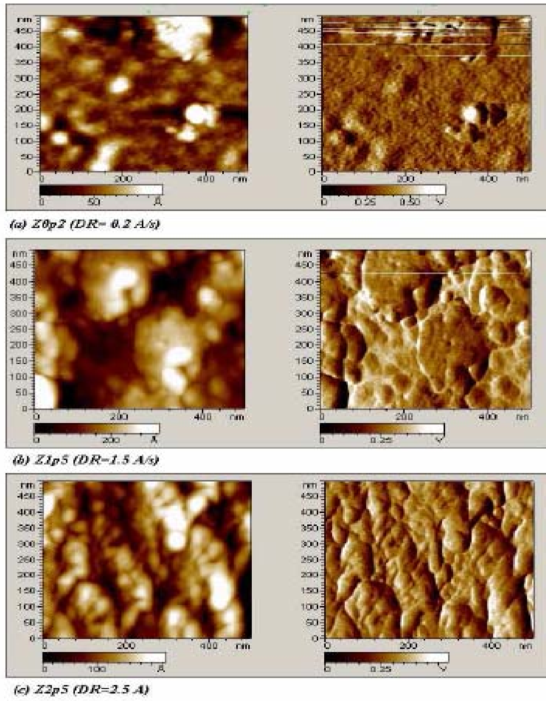

Figure1. Topographical and Phase Modulated AFM Images in (500 nm)^2 Scan Area.

Measurements: In order to obtain unbiased structural characterization data, images were obtained at three different scan areas, each being around 0.5 mm away from each other. Measurements were done under ambient conditions (20°C/40% RH) using a micro cantilever probe, tip radius and probe spring constant are in the ranges of 5-10 nm and 4-5 N/m, respectively.

Topographic and phase images were obtained simultaneously using a resonance

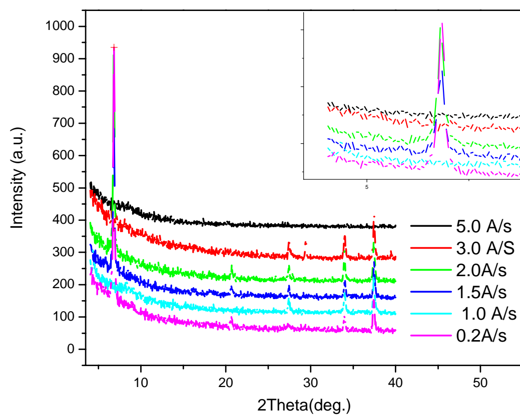

Figure3. X-Ray diffraction data of the sample deposited at different deposition rates

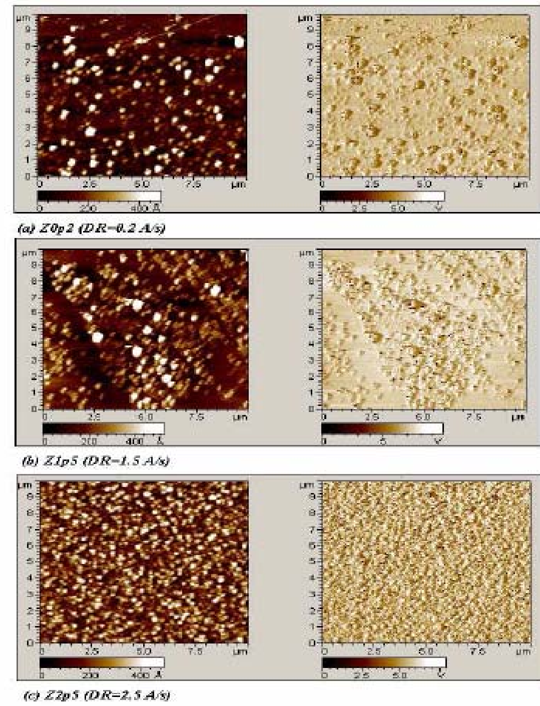

Figure2. Topographical and Phase Modulated AFM Images in (10000 nm)^2 Scan Area.

frequency of approximately 150 kHz for the probe oscillation

For photoluminescence (PL) measurements, the slit width used was 2.00mm and the integration time was kept at 0.1s. These parameters were unchanged during the whole measurement. The excitation energy for obtaining PL spectrum was kept in the region around HOMO-LUMO gap(~2.7 eV). Photoluminescence Excitation spectrum and Time resolved photoluminescence experiments were also performed on all the samples.

A photo-elastic Phase modulated Spectroscopic Ellipsometer (UVISEL, Jobin Yvon Horiba) was used for the Ellipsometric measurements at 70° fixed angle between the Analyzer and Polarizer. The intensity $I(t)$ is given by:

$$I(t) = C(I_o + I_s \sin d(t) + I_c \cos d(t))$$

(1)

The measured raw data Io, Is and Ic are functions of Y, D, and the angles A, P and M of the analyzer, polarizer and modulator being referred to the plane of incidence. Y and D may be calculated from these measurements along with our configuration M=0° and $A=\pm 45^o$ with $PM=\pm 45^o$. Using Marquard-Levenberg algorithm we can now fit the raw data to a dispersion model, the resultant best fit dispersion relations can be estimated by minimizing the value of $\chi 2$.

Results and Discussion

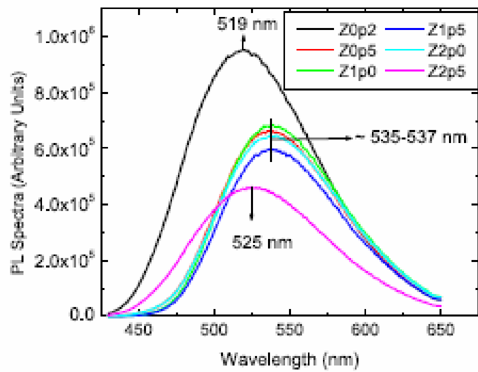

Figure4. Photoluminescence Spectra of ZnQ_2 thin films excited at 375nm deposited at different rates on Si substrates.

AFM images of the thin films are shown in Fig. 1 and Fig. 2. The effects of deposition rates are clearly observed in both the topographical and by contrast in phase images.

The roughness measured by AFM was used as initial parameter for calculating dielectric functions by SE. The obtained RMS roughness averaged over the three different spots are tabulated in Table 1. The error bars indicate the maximum deviation seen among the three places with respect to the average, hence can be an estimation of the minimum and maximum of the values of the thickness for the rough layer in SE modeling.

The x-ray diffraction data is shown in figure 3. A strong diffraction peak exists at $2\theta=6.35^o$ in sample deposited at lower rates.

The photoluminescence are shown in figure 4. The results are quite close to that reported in literature[8,10]. In our case we obtained the PL emission maxima at 536nm and two PL excitation peaks at 344nm and 375nm respectively.

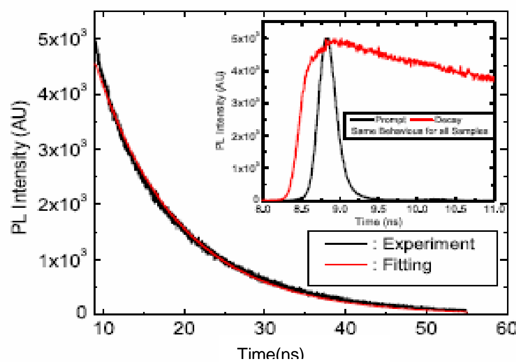

Figure5. TRPL spectra of ZnQ2 on glass substrate. Samples of all deposition rates show identical decay dynamics. Fitting is done with single exponential function luminescence Spectra excited at 370nm.

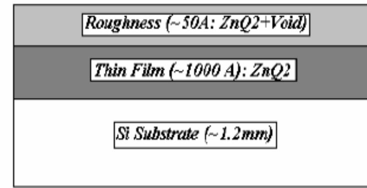

Figure6. Model Used for Ellipsometric Fitting of parameters using Marquardt-Levenberg Algorithm. The model consists of 50A rough surface, modeled by ZnQ_2 and Void on top of a 1000A ZnQ_2 film deposited on a Si wafer of all Deposition rates.

The red shift of PL maxima from 0.2 A/s to higher deposition rates are due to the formation of anhydrous crystalline tetramer $[ZnQ2]_4$. As the temperature required for higher deposition rate increases there is more conversion of the dihydrate into its tetramer. Similar red shift was also obtained by Bing-She [8] by vacuum annealing. This again is attributed to the lowering of

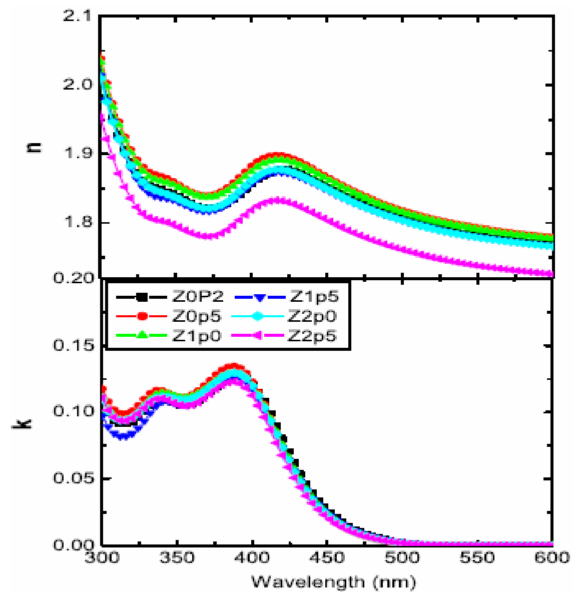

Figure7. Refractive index of ZnQ2 films.Tauc-Lorentz model was using experimental SE data.

LUMO level.

An interesting aspect of the PL spectra is that the PL peak again shifts back to blue side (518 nm peak) at very high deposition rates. Results from PL spectra suggest that the deposition rate must be maintained between 0.5 to 2.0 A/s for obtaining the anhydrous ZnQ_2 properties. Lower rates inhibit conversion of $ZnQ_2.2H_2O$ into anhydrous ZnQ_2.

We measured the time resolved photoluminescence spectra and the results obtained are shown in Fig. 5. All

our samples gave exactly overlapping spectra indicating same intramolecular interaction. The fitting is done using a single exponential decay

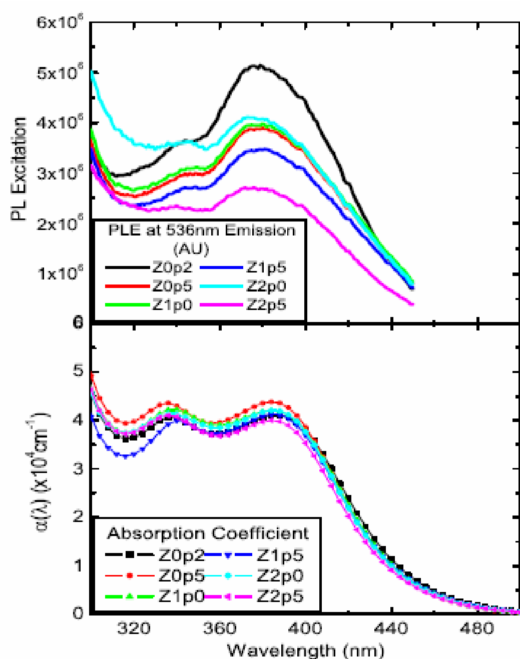

Figure8. Experimentally obtained PL Excitation spectra and modeled absorption coefficient α (λ).

The decay time obtained was 10.31±0.01 ns. This is in close agreement with AlQ_3 thin films. We incorporate the effect of roughness on the film by using a model shown in Fig. 6.

We begin the fitting by making a better estimation of thickness by using the non-absorbing part of the spectrum. This low energy (1.6-2.5 eV) region was fitted to a Cauchy-Transparent dispersion model with only two parameters. The initial values of the parameters were chosen by repeated analysis to be A=1.6421 and B=4.4077. The AFM roughness results were used with a 50% void in Brugmann EMA (Effective Medium Approximation). The initial thickness was chosen from the AFM roughness results. The obtained fitted thickness values were then used for further analysis. Fitting for the dispersion relations were using Tauc-Lorentz model having three oscillators in the range 1.5-4.5eV. The results obtained are shown in Fig. 7.

We experimentally obtained PL Excitation spectra which showed close agreement to our modelled absorption coefficient [$\alpha(\lambda) = 4\pi(\lambda) / \lambda$] shown in Fig. 8. Apart from the singlet-singlet absorption, Both PLE and modelled α(λ) showed the presence of two absorption peaks around 340nm and 380nm.

Conclusion

Optical properties of ZnQ_2 thin films on Si substrates revealed that the films formed are both dihydrate and anhydrous in nature. The shift in the PL spectra at different deposition rates also points to the change in the optical band gap by lowering of LUMO level due to the formation of anhydrous $(ZnQ_2)_4$ with a PL maxima at 536nm. The better films were obtained at deposition rates between 1.0 - 2.0 A/s. TRPL revealed similar intramolecular interactions. SE modeling was done taking into account the roughness of the films by using Brugmann EMA. The n-k dispersion relations were obtained by TL model fitting and are reported.

Acknowledgement

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