Eur. Phys. J. Appl. Phys. **31**, 179–183 (2005)
DOI: 10.1051/epjap:2005063

THE EUROPEAN PHYSICAL JOURNAL
APPLIED PHYSICS

Optical constants of 2,3-bis-(N,N-1-naphthylphenylamino) -N-methylmaleimide thin film by spectroscopic ellipsometry

W. Xie[a], C. Li, and S. Liu

National Laboratory of Integrated Optoelectronics, Jilin University, Changchun, 130012, China

Received: 4 February 2005 / Received in final form: 18 May 2005 / Accepted: 8 June 2005
Published online: 14 September 2005 –

Abstract. Optical constants of 2,3-bis-(N,N-1-naphthylphenylamino)-N-methylmaleimide (NPAMLI) thin film grown on silicon substrate by thermal evaporation were investigated using variable angle spectroscopic ellipsometry (VASE). Accurate refractive index n and extinction coefficient k are reported in the energy range of 1.0 to 5.0 eV. Cauchy model, one-oscillator Lorentz model, and six-oscillator Lorentz model were used to fit the experiment data. The optical gap of NPAMLI and the visible absorption peaks at 2.35 and 2.87 eV were also derived from the VASE spectrum.

PACS. 29.30.-h Spectrometers and spectroscopic techniques – 78.20.Ci Optical constants – 78.66.Qn Polymers; organic compounds

1 Introduction

Organic light-emitting devices (OLEDs) have been studied intensively since Tang and VanSlyke reported a low-voltage, high-efficiency device in 1987 [1]. Red OLEDs with high brightness and high color purity are necessary for the development of organic full color displays. Concentration quenching is a serious problem for red OLEDs. Doping is a universal method for solving the concentration quenching problem of these red-emissive materials in OLEDs [2–5]. However, the doping system shows a contrary phenomenon of low efficiency at high concentration of dopant or poor color purity at low concentration of dopant. Currently, a novel new material 2,3-bis-(N,N-1-naphthylphenylamino)-N-methylmaleimide (NPAMLI) that is a molecular glass material acted as red emitter has been reported [6]. The maximum external quantum efficiency (η_{ext}) of the non-doped type red OLEDs based on NPAMLI can achieve 2.4%. However, the optical constants that are needed for optimizing the design of the device of this new material are unknown.

Optical constant measurements of the organic materials such as N'-bis-(1-naphthyl)-N,N'-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB) [7], tris-(8-hydroxyquinoline) aluminum (Alq_3) [7–10], and poly(2-methoxy-5-(2'-ethylhexyloxy)-p-phenylenevinylene) (MEH-PPV) [11], have been reported by spectroscopic ellipsometry. In this paper, optical constants of NPAMLI thin film, including the refractive index n and extinction coefficient k, were measured using variable angle spectroscopic ellipsometry (VASE) over the wavelength range 1.0–5.0 eV. The band gap of the NPAMLI is also derived from the VASE spectrum.

2 Spectroscopic ellipsometry

The mathematical theory for ellipsometric analysis is based on the Fresnel reflection or transmission equations for polarized light encountering boundaries in planar multilayered materials. The ellipsometric measurement is normally expressed in terms of Psi (Ψ) and Delta (Δ):

$$\tan(\Psi) \cdot e^{i\Delta} = \rho = \frac{r_p}{r_s} \tag{1}$$

where r_p and r_s are the complex Fresnel reflection coefficients of the sample for p- (in the plane of incidence) and s- (perpendicular to the plane of incidence) polarized light. SE measures the complex ratio ρ as a function of wavelength. VASE performs the above measurement as a function of both wavelength and angle of incidence. An optical model for the sample under study is constructed after data are acquired covering the desired spectral range and angles of incidence. Then the model parameters to be varied in order to fit the experimental data are specified. The Mean Squared Error (MSE) is used to quantify the difference between the experimental and predicted data. A smaller MSE implies a better model fit to the data. The MSE function commonly used is given by

$$MSE = \sqrt{\frac{1}{2N-M}\sum_{i=1}^{N}\left[\left(\frac{\Psi_i^{Mod}-\Psi_i^{Exp}}{\sigma_{\Psi,i}^{Exp}}\right)^2+\left(\frac{\Delta_i^{Mod}-\Delta_i^{Exp}}{\sigma_{\Delta,i}^{Exp}}\right)^2\right.} \tag{2}$$

[a] e-mail: xiewenfa@mail.edu.cn

where N is the number of Ψ-Δ pairs, and M is the number of variable parameters used in the model.

3 Experimental details

The red emitting material of NPAMLI was purchased from Academia Sinica. The organic film layer was deposited on silicon wafer because of the higher reflectance of the substrate and hence higher accuracy in obtaining the reflectance data. Prior to the organic layer deposition, the substrate was cleaned by scrubbing and sonication. Then substrate was followed by rinsing in DI water and N_2 drying. The organic layers were deposited by vacuum deposition at 10^{-6} torr using resistively heated tantalum and quartz boats. The substrate was rotated during evaporation to enhance the film thickness uniformity. The NPAMLI film was deposited at a rate of 1–2 Å/s. The thicknesses of layers were controlled by quartz-crystal monitor. Ellipsometric measurements were carried out at room temperature at four angles of incidence (55°, 60°, 65° and 70°) in the photon energy range of 1.0–5.0 eV, using a computer-controlled variable angle spectroscopic ellipsometer from Woollam Company. Data acquired at different angles were fitted simultaneously to minimize instrumentation error. The ellipsometry data was fitted by the software WVASE32.

4 Results and discussion

First, the optical constants of NPAMLI thin film were modeled in the transparent region below 2.0 eV, where k is negligible and n can be adequately fitted by the Cauchy equation:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \quad (3)$$

where A, B, and C are fitting parameters and λ is the wavelength of incident light. Figure 1 shows Ψ and Δ for NPAMLI, together with the fit obtained. All the best-fit parameter values and the 90% confidence limit of each parameter are list in Table 1.

When we extended the fitting range to higher energy, the *MSE* became much larger. Figure 2 shows the best-fit results. It can be seen that the Cauchy model is inaccurate above 2.0 eV. It is indicated that there are absorption bands in the range above 2.0 eV.

An accurate determination of the film thickness and optical constants of NPAMLI can be achieved by modeling the data with one- or more-oscillator Lorentz oscillator model (LOM) of the form

$$\tilde{\varepsilon}(h\upsilon) = \varepsilon_1 + i\varepsilon_2 = \varepsilon_{1\infty} + \sum_k \frac{A_k}{E_k^2 - (h\upsilon)^2 - iB_k h\upsilon} \quad (4)$$

where $\varepsilon_{1\infty}$ is an additional offset term defined in the model. For the kth oscillator, A_k is the amplitude, E_k is the center energy, B_k is the broadening of each oscillator, and $h\nu$ is the photon energy in eV. One-oscillator LOM

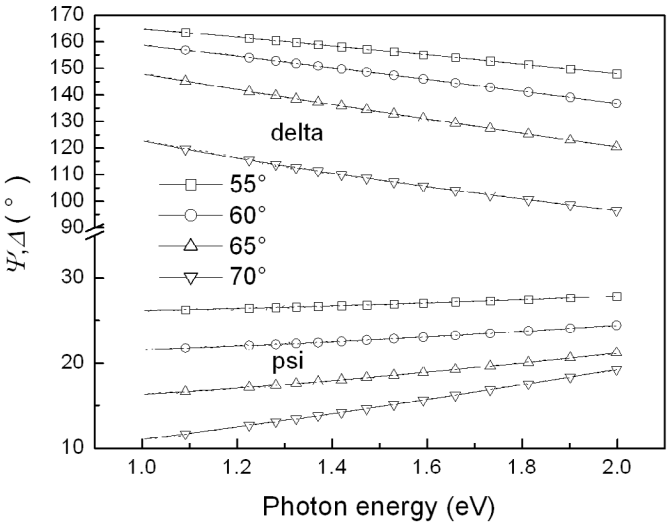

Fig. 1. Measured Ψ and Δ (dash lines) and the Cauchy model fit (solid lines) for VASE at the energy range from 1.0 to 2.0 eV.

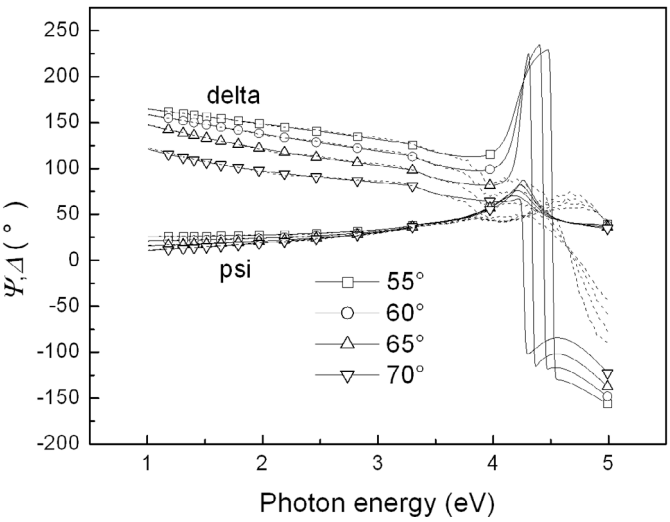

Fig. 2. Measured Ψ and Δ (dash lines) and the Cauchy model fit (solid lines) for VASE at the energy range from 1.0 to 5.0 eV.

was first used to fit the data in the whole energy range from 1.0 to 5.0 eV. Figure 3 shows the best-fit results and the best-fit parameter values is list in Table 2. Though the *MSE* is smaller than that of the Cauchy model, the results of one-oscillator LOM fit are insufficient yet, especially in the range below 3.6 eV.

Then we tried to use more-oscillator LOM to fit the whole data range. Best fitting was obtained with a *MSE* of 2.161 when a six-oscillator LOM is used to fit and a seven-oscillator LOM was attempted but no significant improvement of the fitting was achievable. Figure 4 shows the best-fit results. The best-fit parameter values are given in Table 3. It can be seen that the fitting results agreed well with the experimental data in the whole measurement range.

Table 1. Best-fit parameter values and 90% confidence limit resulting from Cauchy model fit.

	A	B (nm^2)	C (nm^4)	Thickness (nm)	*MSE*
Value	1.6669	0.0683	–0.0021	33.884	1.145
90% confidence limit	0.0071	0.0065	0.0017	0.070	

Table 2. Best-fit parameter values and 90% confidence limit resulting from one-oscillator LOM fit.

	$\varepsilon_{1\infty}$	A_1 (eV)^2	B_1 (eV)	E_1 (eV)	Thickness (nm)	*MSE*
Value	1.4224	103.22	4.8929	8.8079	34.779	7.86
90% confidence limit	0.1800	1.800	0.3410	0.4540	0.1020	

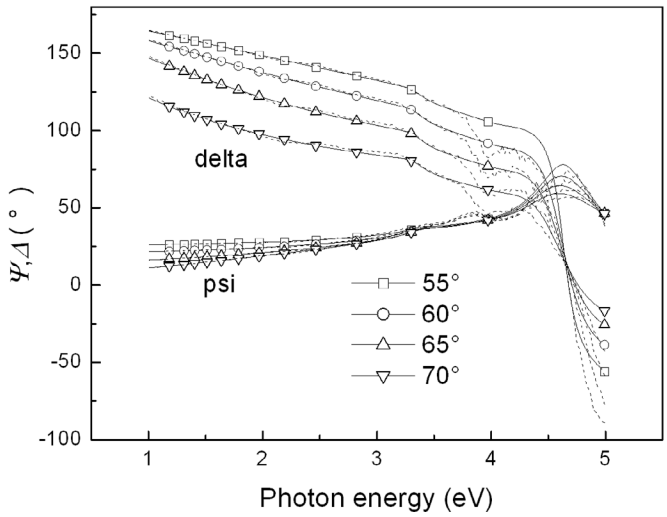

Fig. 3. Measured Ψ and Δ (dash lines) and the one-oscillator LOM fit (solid lines) for VASE at the energy range from 1.0 to 5.0 eV.

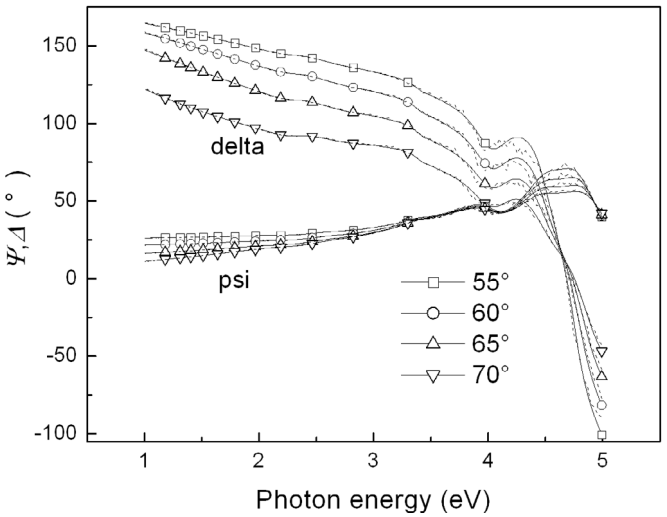

Fig. 4. Measured Ψ and Δ (dash lines) and the six-oscillator LOM fit (solid lines) for VASE at the energy range from 1.0 to 5.0 eV.

In Figure 5 are shown the refractive index and extinction coefficient as derived from a six-oscillator LOM fit. From the extinction coefficient, the absorption coefficient $\alpha = 4\pi k/\lambda$ can be calculated. The visible absorption peaks at 2.35 and 2.87 eV were derived from the absorption spectrum. The maximum absorption peak at visible region is 2.35 eV, that is 527 nm.

NPAMLI is an organic amorphous semiconductor. Because of the presence of localized states at energies between valence and conduction bands, the optical gap E_g is an ill-defined parameter in amorphous semiconductors. Several ways are currently in use to define E_g in amorphous semiconductors. The simplest one is to consider E_g as the energy corresponding to an absorption coefficient of 10^3 cm^{-1} (E_{03}) of 10^4 cm^{-1} (E_{04}). Generally, accurate spectroscopic ellipsometry measurements of α can only be made for values of $\alpha \gtrsim 10^4$ cm^{-1}. If we define $E_g = E_{04}$, then the optical band of NPAMLI is 2.04 eV. Another usual definition of E_g in amorphous semiconductors is the so-called Tauc's equation [12]

$$[\alpha(\lambda)h\upsilon]^{1/2} = C^{1/2}(h\upsilon - E_g) \tag{5}$$

where C is a proportional constant independent of photon energy and $C^{1/2}$ gives a measure of disorder effect in band edge. Figure 6 shows the behavior of absorption at photon energies above the exponential region. Straight lines are obtained on the plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ and optical band gap of about 1.9 eV at room temperature can be obtained by extrapolation. An EL spectrum with an emission maximum at 650 nm, that is 1.908 eV, was observed in the non-doped type red OLED [6].

This value is very closed to that obtained by SE measurement. We also used cyclic voltammetry (CV) to measure the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of NPAMLI. The measured HOMO and LUMO levels were 5.8 and 3.9 eV, respectively, which gave a band-gap

Table 3. Best-fit parameter values resulting from six-oscillator LOM fit, the value in bracket is the 90% confidence limit.

Oscillator	A_k $(\text{eV})^2$	B_k (eV)	E_k (eV)	$\varepsilon_{1\infty}$	Thickness (nm)	*MSE*
1	0.3793 (0.0073)	0.3240 (0.0056)	2.3330 (0.0017)			
2	0.2945 (0.0171)	0.5156 (0.0285)	2.8693 (0.0067)			
3	0.0308 (0.0025)	0.1027 (0.0554)	3.4486 (0.0188)	2.374 (0.037)	34.27 (0.0153)	2.161
4	1.3151 (0.0205)	0.4349 (0.0393)	4.1144 (0.0108)			
5	2.7798 (0.6580)	0.7770 (0.1100)	4.6198 (0.0159)			
6	11.642 (0.5600)	0.2927 (0.0894)	5.5095 (0.0568)			

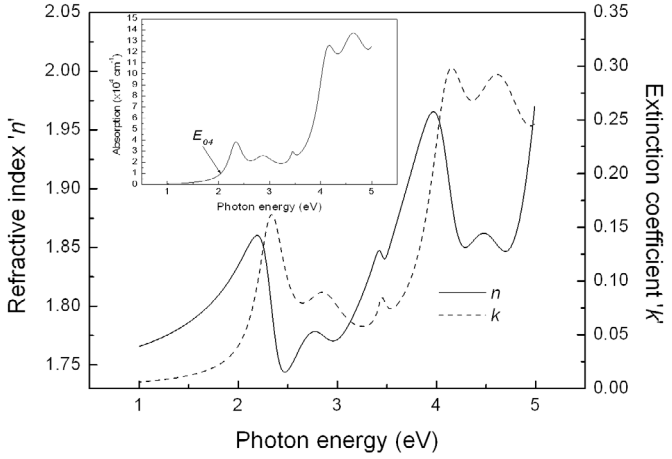

Fig. 5. Refractive index and extinction coefficient of NPAMLI obtained by six-oscillator LOM fit. Inset is the absorption spectra calculated from extinction coefficient.

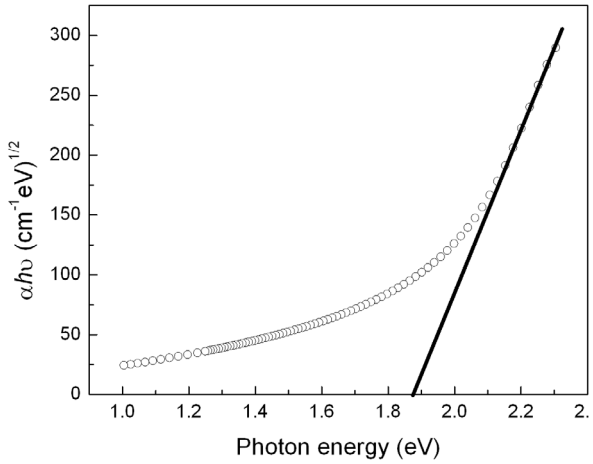

Fig. 6. Fitting of the absorption edge data to the amorphous semiconductors model.

energy of 1.9 eV. This value is equal to that obtained by SE measurement. The value of C, which is 5.0×10^5 cm^{-1} eV^{-1}, was also obtained. This value is similar to those of many amorphous semiconductors [13].

The external quantum efficiency of an LED is the product of internal quantum efficiency of the photon extraction efficiency. For OLEDs, Kim et al. pointed out the efficiency should be $0.75/n^2$ to $1.2/n^2$, depending on the alignment conditions of emitting dipoles [14]. Red light with a peak wavelength at 650 nm was obtained from the OLED using NPAMLI as red emitting material. The refractive index of the NPAMLI is n (650 nm)=1.82 from the fitting data. Using the average figure of $1/n^2$ and assuming the singlet:triplet branching ratio is 1:3, the maximum external quantum efficiency of the NPAMLI OLED should be 7.2% that is higher than the experiment data of 2.4%. This indicated that there is more scope to improve the performance of OLED based on NPAMLI.

5 Conclusion

We have used variable angle spectroscopic ellipsometry to investigate the optical constants of a novel material NPAMLI, which will be useful in red OLEDs, grown on silicon substrate by thermal evaporation. The VASE data were model by using Cauchy model, one-oscillator LOM and six-oscillator LOM in different energy ranges. Accurate refractive index and extinction coefficient in the energy range from 1.0 to 5.0 eV were obtained. The maximum visible absorption peak is 527 nm. The optical gap of 1.9 eV using Tauc's equation or 2.04 eV at the absorption coefficient of 10^4 cm^{-1} is also derived.

This work was supported by the National Natural Science Foundation of China under Grant Nos. 60207003 and 60376028 and National "973" project of China under Grant No. 2003cb314703.

References

1. C.W. Tang, S.A. VanSlyke, Appl. Phys. Lett. **51**, 913 (1987)
2. C.W. Tang, S.A. VanSlyke, C.H. Chen, Appl. Phys. Lett. **65**, 3610 (1989)
3. Z.Y. Xie, L.S. Hung, S.T. Lee, Appl. Phys. Lett. **79**, 1048 (2001)
4. Y.D. Jin, J.P. Yang, P.L. Heremans, M.V. Auweraer, E. Rousseau, H.J. Geise, G. Borghs, Chem. Phys. Lett. **320**, 387 (2000)
5. J. Feng, F. Li, W.B. Gao, G. Cheng, W.F. Xie, S.Y. Liu, Appl. Phys. Lett. **81**, 2935 (2002)
6. W.C. Wu, H.C. Yeh, L.H. Chan, C.T. Chen, Adv. Mater. **14**, 1072 (2002)
7. W.F. Xie, Y. Zhao, J.Y. Hou, S.Y. Liu, Jpn J. Appl. Phys. **42**, 1466 (2003)
8. E.G. Celii, T.B. Harton, O.F. Phillips, J. Electron. Mater. **26**, 366 (1997)
9. B. Maseneli, S. Callard, A. Gagnaire, J. Joseph, Thin Solid Films **364**, 264 (2000)
10. A.B. Djurišić, C.Y. Kwong, T.W. Lau, E.H. Li, Z.T. Liu, H.S. Kwok, L.S.M. Lam, W.K. Chan, Appl. Phys. A **76**, 219 (2003)
11. M. Tammer, A.P. Monkman, Adv. Mater. **14**, 210 (2002)
12. J. Tauc, R. Grigorocivi, A. Vancu, Phys. Status Solidi **15**, 627 (1966)
13. N.F. Mott, E.A. Davis, *Electronic processes in non-crystalline materials* (Clarendon, Oxford, 1979)
14. J.S. Kim, P.K. Ho, N.C. Greenham, R.H. Friend, J. Appl. Phys. **88**, 1073 (2000)