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Characterization of Poly(9-vinylcarbazole) and 8-Hydroxyquinoline Aluminum Using a Homemade Rotating Analyzer Ellipsometer

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Abstract: In this work we use a homemade spectroscopic ellipsometer to study two commonly used organic materials; namely poly(9-vinylcarbazole) (PVK) and 8-hydroxyquinoline aluminum (Alq_3). The ellipsometric parameters ψ and Δ are measured as a function of the wavelength. Fresnel's equations are then inverted to obtain the optical parameters and the thickness of these samples. The dispersion of the refractive index of Alq_3 and PVK thin films is found to obey Cauchy's equation.

Keywords: Rotating analyzer ellipsometer, PVK, Alq_3.

دراسة الخصائص الضوئية لــ poly(9-vinylcarbazole) and 8-hydroxyquinoline aluminum باستخدام مقياس الاستقطاب الطيفي المصنع محلياً

الملخص: نستخدم مقياس الاستقطاب الطيفي المصنع محلياً لدراسة الأفلام الرقيقة لمادتين عضويتين شائعتي الاستخدام وهما poly(9-vinylcarbazole) (PVK) and 8-hydroxyquinoline aluminum (Alq_3)، نقوم بقياس معاملات مقياس الاستقطاب الطيفي كدوال في الطول الموجي للضوء الساقط على العينة، ثم نستخدم معادلات فرينل لحساب المعاملات الضوئية وسمك هذه الأفلام، وكذلك وجد أن انتشار معامل الإنكسار يتبع معادلة كوشي لكل عينة.

1. Introduction

Ellipsometry in different forms has been used for several centuries [1-6]. The most general meaning of ellipsometry is the measurement and analysis of elliptical polarization of light. Recently, ellipsometry is studied extensively as a non-destructive technique for characterization of bulk solids and thin films.

An ellipsometer measures the change in the polarization state of incident light. If a linearly polarized light of known orientation is reflected from a surface, then the reflected light will be elliptically polarized. The shape and the orientation of the ellipse depend on the angle of incidence, the direction of the polarized incident light, and the reflection properties of the surface. Two parameters $\tan\psi$ (the ratio of the amplitudes of Fresnel's reflection coefficients) and Δ (phase change between p- and s-polarized lights) are determined in one single ellipsometric measurement. This makes it possible to obtain both the real and imaginary parts of the complex dielectric function of a homogeneous material. The fundamental ellipsometric equation is conventionally written as

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

where r_p and r_s are the complex Fresnel's reflection coefficients which may be written as

$$\left.\begin{aligned} r_p &= |r_p| e^{i\delta_p} \\ r_s &= |r_s| e^{i\delta_s} \end{aligned}\right\}, \tag{2}$$

where δ_p and δ_s are the phase changes the *p* and the *s* components of light undergo upon reflection.

The value of ψ can range from 0 to 90° and is written as

$$\tan(\psi) = \frac{|r_p|}{|r_s|} = \frac{|r_p|}{|r_s|}. \tag{3}$$

The angle Δ is the phase difference between the two components p and s induced by reflection. It can have the values between 0 to 360° and is written in the form

$$\Delta = \delta_p - \delta_s. \tag{4}$$

The two angles ψ and Δ are measured experimentally using an ellipsometer. Once, ψ and Δ are determined during a measurement at a given wavelength one can invert Fresnel equations to extract the optical parameters of a bulk sample. For a substrate/thin film/ambient structure one should measure ψ and Δ at several wavelengths to obtain all parameters of the thin film.

In the last twenty years, ellipsometry has become a widely used method in fundamental research as well as commercial fields like production, quality control, real time monitoring of surfaces and thin films during processing.

Thin organic films have many attractive features and are being widely investigated by researchers for use in electronic devices [7-11]. The main advantage of organic materials over inorganic semiconductors is that they can be deposited by evaporation, spin-coating, screen printing, and casting. These deposition techniques are simpler and cheaper than most of the deposition methods used in inorganic semiconductors. Among the mostly used organic materials are poly(9-vinylcarbazole) (PVK) and 8-hydroxyquinoline aluminum (Alq_3). They have been used in many applications such as organic light emitting diodes [12-14]. The structures of PVK and Alq_3 are shown in Fig. 1.

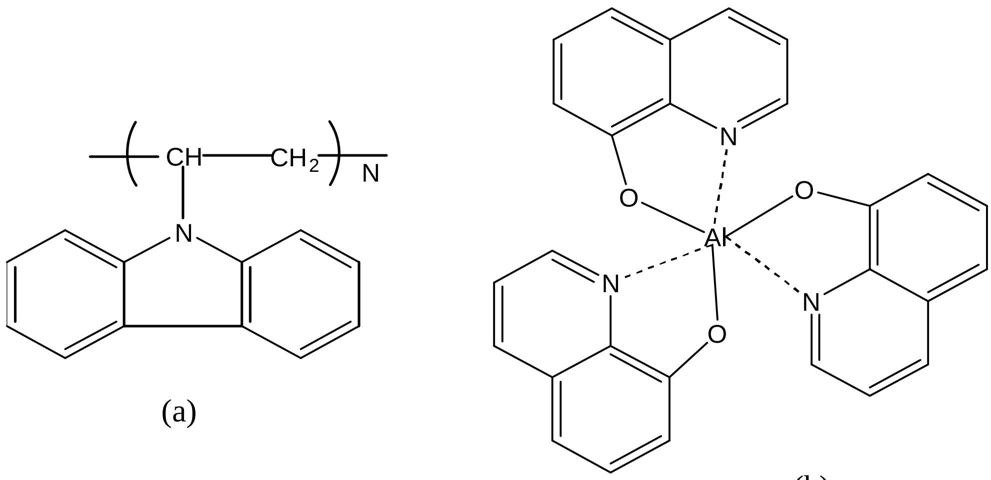

Fig. 1. The structures of (a) PVK and (b) Alq_3.

In this work we study the optical properties of PVK and Alq_3 films deposited on Si wafer using a homemade spectroscopic ellipsometer. We investigate the dispersion properties of these materials in the visible spectrum. The ellipsometric parameters ψ and Δ are obtained using the Fourier transform of the signal received by the detector. The optical parameters and the thickness of these samples are then calculated using Fresnel equations.

2. Ellipsometer description

The ellipsometer under consideration was constructed at Physics Department of the Islamic University of Gaza. The main components of the ellipsometer are shown in Fig 2. It consists of the following elements: 1) halogen tungsten lamp as the light source, 2) Lens assembly to collect the largest amount of light, 3) An aperture, 4) Monochromator to obtain a semi-monochromatic light, 5) A single double convex lens to collect light from the monochromator and focus it to a pinhole, 6) Reference pinhole, 7) A single double convex lens, 8) Polarizer model MGTYE10 made by KARL LAMBRECHT, 9) A circular disk attached to the barrel of the polarizer to define the home position of the polarizer, 10) Rotating polarizer, 11) Sample holder, 12) A circular disk attached to the barrel of the analyzer to define the home position of the analyzer, 13) Rotating analyzer, and 14) Photomultiplier tube (PMT).

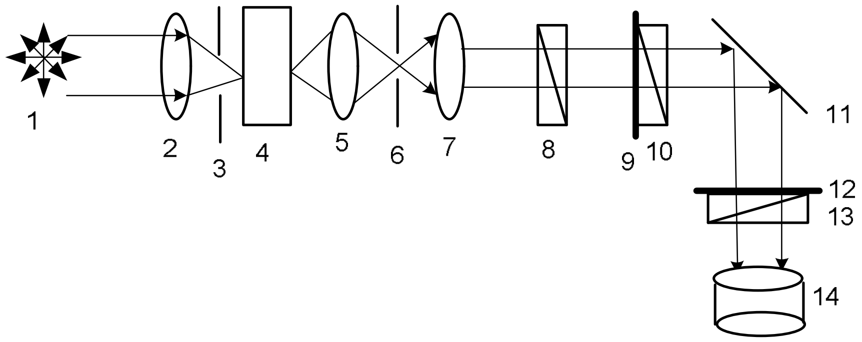

Fig. 2. A schematic diagram of the homemade ellipsometer under consideration.

In this work, we have used a rotating analyzer ellipsometer in which the polarizer was held fixed while the analyzer was rotating continuously during the measurements. For such ellipsometer the state of polarization before striking the sample is linear and is elliptical upon reflection. The polarization state of the reflected light becomes linear after passing through the rotating analyzer. The direction of polarization varies in time at the detector which measures the intensity as a function of time. The PMT detects sinusoidally time dependent intensity *I(t)*. It records different intensities at different states of polarization [15,16]. A Fourier analysis of the sine wave can be used to find the values of the ellipsometric parameters

$$I(t) = I_0[1 + a\cos(2wt) + b\sin(2wt)], \qquad (5)$$

where, I_0 is the average intensity, α and β are the Fourier coefficients of the intensity and w is the angular speed of the rotating analyzer. The Fourier coefficients of the intensity are related to the ellipsometric parameters ψ and Δ by

$$a = \frac{\tan^2(y) - \tan^2(P)}{\tan^2(y) + \tan^2(P)}, \qquad (6)$$

$$b = \frac{2\tan(y)\cos(D)\tan(P)}{\tan^2(y)+\tan^2(P)}, \qquad (7)$$

where P is the fixed polarizer angle

The ellipsometric parameters ψ and Δ can be deduced from the Fourier coefficients as

$$\tan(y) = \sqrt{\frac{1+a}{1-a}}\left|\tan(P)\right|, \qquad (8)$$

$$\cos(D) = \frac{b}{\sqrt{1-a^2}}\left(\frac{\left|\tan(P)\right|}{\tan(P)}\right). \qquad (9)$$

Once y and Δ are obtained, quadratic equation method [16] can be used to obtain the thickness and the refractive index of thin films.

3. Experimental work

PVK (Sigma-Aldrich, USA) thin films were prepared by dissolving 30 mg of the substance in 15 ml of chloroform. Few drops of the solution were spun at 1750 rpm for one minute to form a thin film on Si wafer. On the other hand, Alq_3 thin films were deposited on Si wafer by thermal vacuum evaporation at $1.7\text{x}10^{-5}$ torr in low rate deposition condition for one minute. Each sample is then mounted in the sample holder (item 11 in Fig. 2) and a beam of light is allowed to impinge on the sample at an incidence angle $\theta_0 = 75^o$. Ellipsometric data were taken at room temperature. The data were recorded and saved as an ASCII file and then were analyzed using a Mathcad code.

4. Results and calculations

Figures 3 and 4 illustrate the variations of the ellipsometric parameters ψ and Δ for an Alq_3 thin film with visible spectrum of wavelengths, respectively. Similarly, Figs. 5 and 6 show, respectively, the variation of the ellipsometric parameters ψ and Δ for a PVK thin film in the same range of wavelengths.

The model of the structure under consideration consists of a thin film (PVK or Alq_3) of refractive index n_1 sandwiched between an ambient (air) of refractive index n_0 and a Si substrate of refractive index n_2. Figure 7 shows a schematic diagram for the structure.

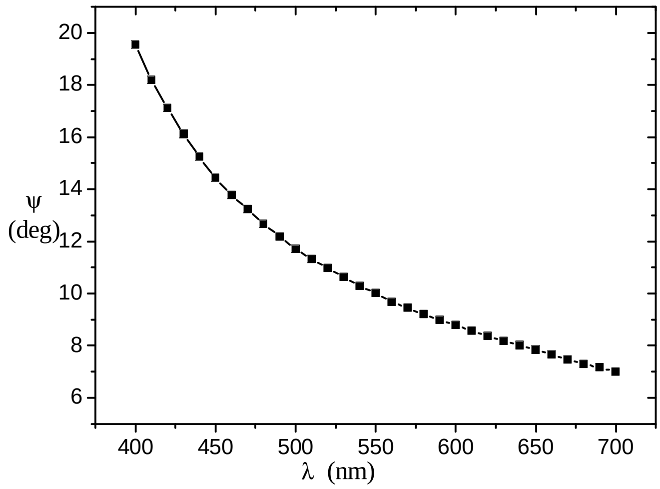

Fig. 3. Variations of *ψ* with λ from 400 to 700 nm for Alq_3 film on a Si wafer at 75^o angle of incidence.

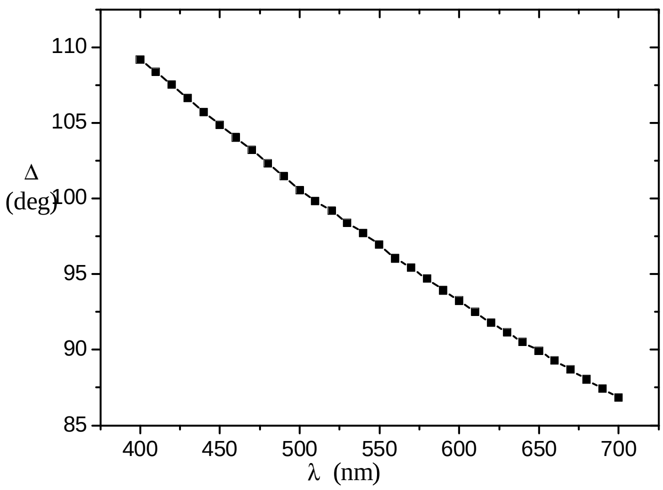

Fig. 4. Variations of *Δ* with λ from 400 to 700 nm for Alq_3 film on a Si wafer at 75^o angle of incidence.

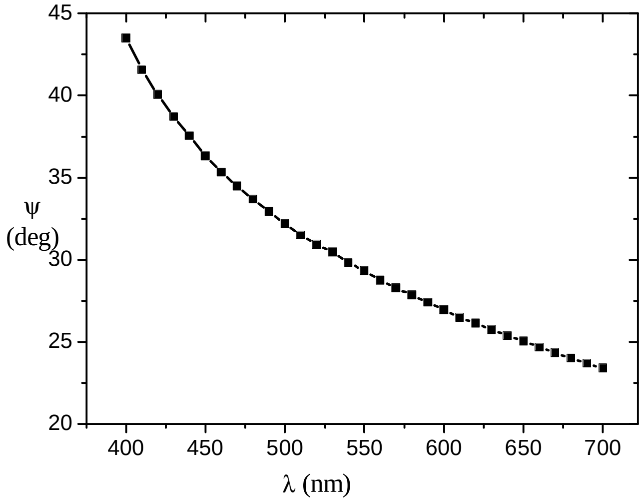

Fig. 5. Variations of *ψ* with λ from 400 to 700 nm for PVK film on a Si wafer at 75^{o} angle of incidence.

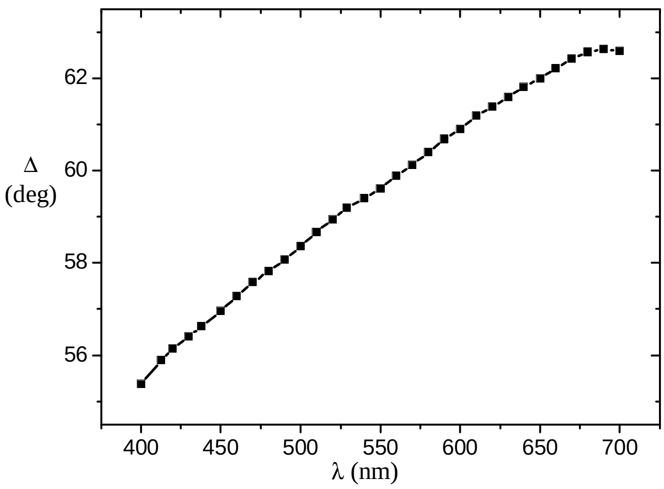

Fig. 6. Variations of *Δ* with λ for PVK film on a Si wafer at 75^{o} angle of incidence.

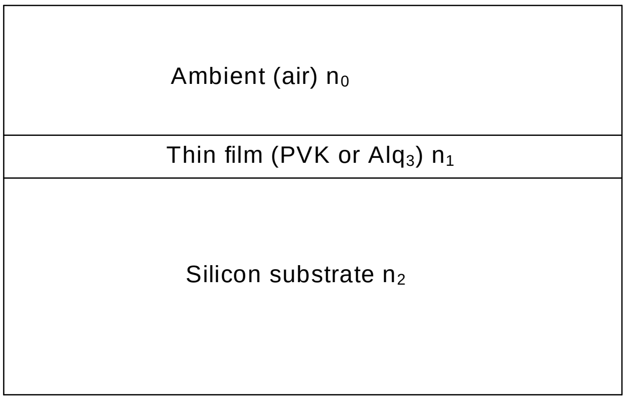

Fig. 7. A thin film of Alq_3 or PVK is sandwiched between an ambient (air) and a Si substrate.

The Fresnel reflection coefficients of this system are given by [1]

$$r_j = \frac{r_{01j} + r_{12j}\exp(-i2\beta)}{1 + r_{01j}r_{12j}\exp(-i2\beta)}, \tag{10}$$

where

j stands for p in p-polarized light and for s in s-polarized light,

$$r_{01s} = \frac{n_0\cos(\theta_0) - n_1\cos(\theta_1)}{n_0\cos(\theta_0) + n_1\cos(\theta_1)}, \tag{11}$$

$$r_{12s} = \frac{n_1\cos(\theta_1) - n_2\cos(\theta_2)}{n_1\cos(\theta_1) + n_2\cos(\theta_2)}, \tag{12}$$

$$r_{01p} = \frac{n_1\cos(\theta_0) - n_0\cos(\theta_1)}{n_1\cos(\theta_0) + n_0\cos(\theta_1)}, \tag{13}$$

$$r_{12p} = \frac{n_2\cos(\theta_1) - n_1\cos(\theta_2)}{n_2\cos(\theta_1) + n_1\cos(\theta_2)}, \tag{14}$$

$$\beta = \frac{2\pi h n_1\cos(\theta_1)}{\lambda}, \tag{15}$$

θ_1 and θ_2 are the refraction angles in the thin film and the substrate, respectively, and *h* is the thickness of the thin film.

Using Eqs. (1) and (10), we obtain

$$\rho = \tan(\psi)e^{i\Delta} = \frac{r_p}{r_s} = \left[\frac{r_{01p} + r_{12p}\exp(-2i\beta)}{1 + r_{01p}r_{12p}\exp(-2i\beta)}\right]\left[\frac{1 + r_{01s}r_{12s}\exp(-2i\beta)}{r_{01s} + r_{12s}\exp(-2i\beta)}\right]. \tag{16}$$

This equation can be simplified [16] to give a quadratic equation as

$$Ax^2 + Bx + C = 0\,, \tag{17}$$

where

$$A = \left(r\, r_{01p} - r_{01s}\right)\left(r_{12p} r_{12s}\right), \tag{18}$$

$$B = r_{01p} r_{01s}\left(r\, r_{12p} - r_{12s}\right) + r\, r_{12s} - r_{12p}\,, \tag{19}$$

$$C = r\, r_{01s} - r_{01p}\,, \tag{20}$$

and

$$x = \exp(-2ib)\,. \tag{21}$$

The solutions of the quadratic equation have the conventional form

$$x = \exp(-2ib) = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A}\,. \tag{22}$$

The thickness in terms of x, n_1 and θ_1 is

$$h = \frac{i\, l \ln(x)}{4p\; n_1 \cos(q_1)}\,. \tag{23}$$

In the visible spectrum, we may consider PVK and Alq_3 to be lossless. In this case the extinction coefficients are close to zero i.e. $k \approx 0$. Thus b will be real and hence $x = \exp(-2jb)$ is pure complex. Therefore,

$$\ln|x| = 0\,. \tag{24}$$

Finally, the solution is to look for the value of n_1 that makes

$$\ln|x| = \ln\left|\frac{-B \pm \sqrt{B^2 - 4AC}}{2A}\right| = 0\,. \tag{25}$$

A Mathcad code was used to solve Eq. (25) and to determine the refractive indices of the samples. Figures 8 and 9 illustrate the results obtained for the refractive indices of Alq_3 and PVK thin films, respectively. Inspection of figure 9 at the sodium D line (589.3 nm) indicates that the experimental refractive index of the PVK film is very close to the value provided by Sigma-Aldrich ($n_D^{20} = 1.6830$).

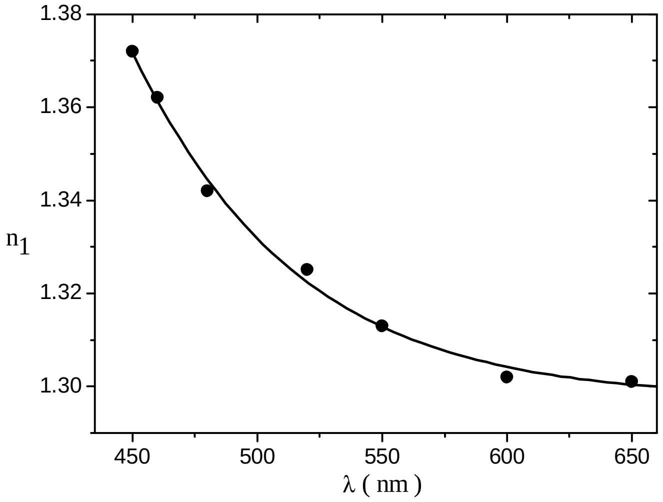

Fig. 8. Dispersion of the refractive index of Alq_3 film on Si substrate with wavelength (visible spectrum) at 75^o angle of incidence.

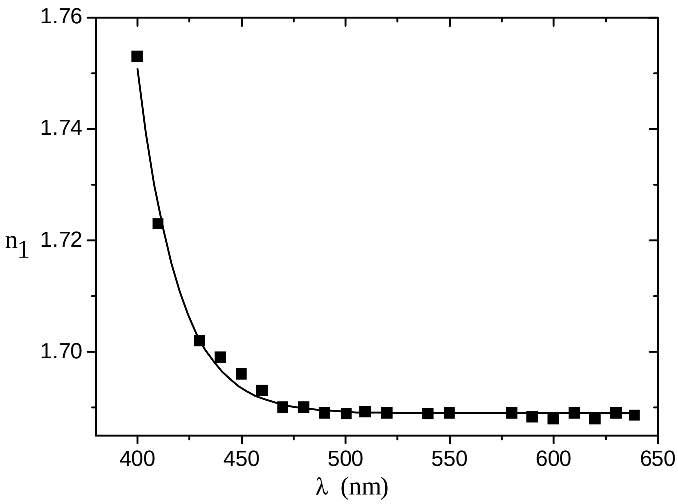

Fig. 9. Dispersion of the refractive index of PVK film on Si wafer with wavelength (visible spectrum) at 75^o angle of incidence.

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The thicknesses of the films were calculated using Eq. (23). We found that Alq_3 and PVK thin films have average thicknesses of 18 nm and 48 nm, respectively.

For pure organic films presented in this work the refractive index (n) decreases slowly with wavelength in the visible spectrum. This dependence can be described with the well known Cauchy relation,

$$n(l) = A + \frac{B}{l^2} + \frac{C}{l^4}, \tag{26}$$

where *A*, *B*, and *C* are called Cauchy parameters. These parameters can be determined for a material by fitting the equation to the measured refractive indices at known wavelength. In our work, the best fit of the experimental data shown in Figs. 8 and 9 according to Eq. (26) gives the values of Cauchy parameters listed in Table I for the samples under consideration.

Table I: Calculated values of Cauchy parameters.

material	**A**	**B ×10^7**	**C×10^{14}**
Alq_3	1.339	-0.3739	0.8915
PVK	1.753	-0.416	0.6267

Conclusion

The variation of the refractive indices with wavelength as well as the thicknesses of two thin films has been determined. The structure under consideration is composed of ambient (air)/thin film (Alq_3 or PVK)/silicon substrate. A homemade rotating analyzer ellipsometer has been used to measure the ellipsometric parameters. Fresnel's equations are then inverted to obtain the optical parameters and the thickness of these samples. The dispersion of the refractive index of Alq_3 and PVK thin films are found to obey Cauchy’s equation.

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