Thin film characterization of novel phthalimide materials

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Spin coating technique is employed to produce thin phthalimide films using novel p-phthalimidobenzoic acid (FIBA) and N-(phthalimido)-p-aminobenzoic acid (FIABA) materials. Several spin speeds and various solution concentrations are chosen to monitor the thin film deposition process of these new materials. The optical properties are studied using UV-visible spectroscopy and spectroscopic ellipsometry methods. The absorption of the FIBA and FIABA films against the spin speed showed an exponential behavior. $\pi \rightarrow \pi^*$ transition is occurred. The thicknesses of thin films at 2000 rpm are obtained 15.86 nm for FIBA and 12.99 nm for FIABA using spectroscopic ellipsometry results.

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1. Introduction

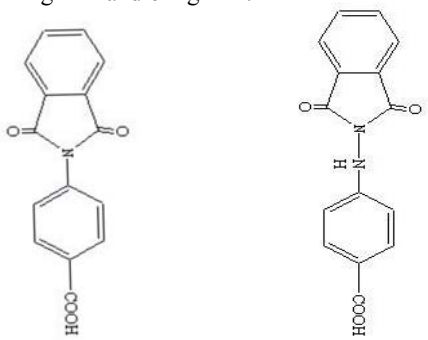
Phthalimides are an imide derivative and solid in room temperatures. They have become of interest in recent years for applications as electrical insulators, alignment films for liquid crystal displays [1], biomaterials as well as in medical and sensor technology [2-5] and electronics [6-8] because of their easy processability, low dielectric constant, their outstanding thermal and mechanical properties.

Phthalimide and phthalamic acids are used for occupational biological monitoring or forensic investigations of the fungicide folpet [9]. Different polyimides such as 5-(2–phthalimidyl–3-methyl butanoylamino) isophthalic molecules exhibit a number of useful properties such as a high thermal stability, high chemical resistance, low flammability with excellent mechanical properties as a fibre [10]. Some studies concerning the fabrication of phthalimides as thin films have shown that the thin film characterization properties depend on the preparation method associated with the physical properties. A slow spin speed brings an increase in the thickness, density and surface properties. Thin film research is an area of great significance in the device fabrication for the advanced technology applications. A simple method for thin film production can be given as a spin coating method. This is a process whereby a small quantity of the desired coating solution is poured onto a substrate that is then rapidly rotated causing the fluid flow radially, with attendant solvent evaporation to leave a uniform thin film. The fluid dynamical aspects of the spin coating process have been extensively reported in the literature [11-12]. Spin coating was extensively used for polymer materials for the fabrication of thin films [13-16].

In the present work, this thin film method is selected to study the thin films of a novel p-phthalimidobenzoic acid (FIBA) and novel N-(phthalimido)-p-aminobenzoic acid (FIABA) materials because there is not much information in the literature on the study of thin film charaterization of phthalimide-based materials. We have characterized the quality as well as the physical properties using UV-visible and spectroscopic ellipsometry methods.

2. Experimental details

The chemical structure of FIBA and FIABA materials are given in Fig. 1. Both materials were dissolved in ethanol with a concentration of 2 mg/ml. Thin films were fabricated on silicon substrate for SE measurement and quartz substrate for UV-visible measurement using a spin coating system (model 4000 from Electronic Microsystems). 50 µl of solution were spread onto a rotating substrate at different spin speeds, in the range 1000- 5000 rpm. For the investigation of concentration dependence, thin films were also prepared at the constant spin speed of 2000 rpm with the different concentrations between 1 mg ml^{-1} and 6 mg ml^{-1}.



(a) (b)

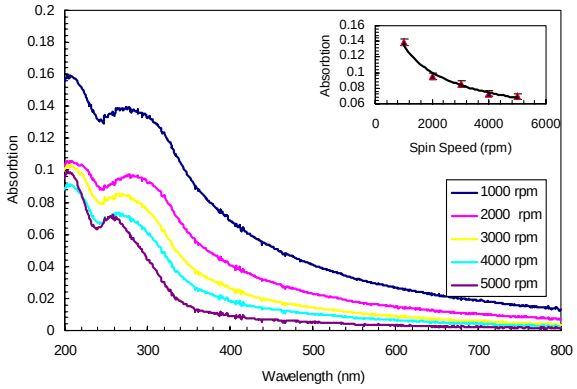
Fig. 1. The chemical structure of two materials investigated: (a) p-phthalimidobenzoic acid (FIBA) and (b) N - (phthalimido) - p - aminobenzoic acid (FIABA).

The UV-visible spectra of LB film were recorded in the region of 200 nm to 800 nm using a Varian CARY 50 spectrophotometer in absorbance mode. After the deposition of FIBA and FIABA thin films onto quartz substrates, UV-vis spectra were recorded as a function of spin speeds.

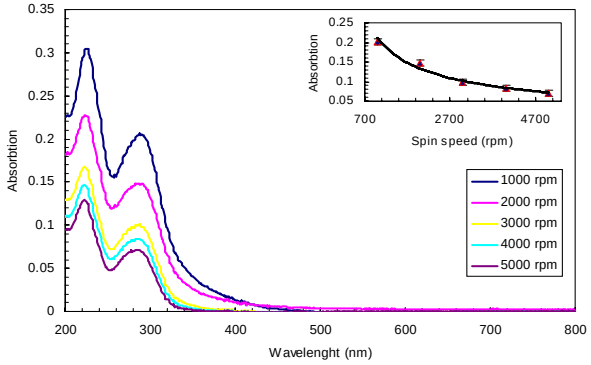
SE measurement system was employed to investigate the film thickness of FIBA and FIABA thin films as a function of spin speed using a silicon substrate. The spectra of two ellipsometric parameters Ψ(λ) and Δ(λ) were recorded with the M2000V instrument in the 350-1000 nm spectral range using the rotating analyzer principle. The data were analyzed with WVASE32 commercial software (provided by J.A.Woollam Co., Inc.) which is the most powerful and comprehensive ellipsometric analysis program for analysis of thin organic films [17]. Using different spin speeds with a solution concentration of 2 mg ml^{-1}, the complete set of parameters such as *d, n*(λ) and *k*(λ) for each layer were obtained by fitting the experimental spectra of Ψ(λ) and Δ(λ) to a particular model.

3. Results and discussion

Fig. 2 and 3 show the UV-visible spectra in the range of 200-800 nm of FIBA and FIABA spun films on quartz substrate with different spinning speeds, ω, (Fig. 2) and solution concentrations, c (Fig. 3). Due to the aromatic π systems and C=O carbonyl group in carboxylic acid structure, molecule exhibits $\pi \rightarrow \pi^*$ transition in B-band [18]. This is clearly evidenced by the remarkable absorption at the wavelengths 280 nm in Fig. 2 (a) and Fig. 3 (a) for FIBA film and at 285 nm in Fig. 2 (b) and Fig. 3 (b) for FIABA film. FIBA molecule also exhibits an absorption peak at the wavelength 205 nm shown in Fig. 2 (a) and Fig. 3 (a). These absorption maxima belong to the $\pi \rightarrow \pi^*$ transition in E_2-band of aromatic system. Absorptions in 223 nm in Fig. 2 (b) and Fig. 3 (b), are caused by E_2-band of the aromatic system of FIABA molecule. The magnitude of a red shift and the increase in absorption intensity are proportional to the electrondonor capacity of the substituent [19]. Comparing FIBA and FIABA spectra, one may suggest the red shift of the B-band and E_2 band of these two molecules (280 to 285 nm and 205 to 223 nm) and the increase in the absorption intensity are based on NH-group in the FIABA molecule.[20]. These results are characteristic for phthalimide derivatives as a film and bulk material and are in good agreement with ones obtained for LB films of fluorine containing poly(amide–imide)s [21] and as bulk materials of N-(3-nitrophenyl)phthalimide [22] and phthalimide dyes [23].



(a)



(b)

Fig. 2. UV-visible absorption spectra graphs of (a) FIBA and (b) FIABA thin films. Both are obtained using 2 mgml^{-1} solution concentration and varying spinning speeds.

Using the UV-visible spectroscopy, the amount of material deposited on the quartz substrate can be investigated in the relation to spin speed and solution concentration. Using Lambert-Beer law, the absorbance, A, can be defined as [24]:

$$A = \log \frac{I_0}{I} = \varepsilon \; b \; c \qquad (1)$$

where *I*: is the intensity transmitted by the sample, I_0: is incident intensity, ε : is the absorption coefficient (L mol^{-1} cm^{-1}), *d*: is the path length (cm) and *c*: is the concentration (mol L^{-1}).

From Eq. 1, the amount of material gives rise to absorbance which related to film thickness or solution concentration. According to the hydrodynamic theory, thickness of the spin coated thin film can be written as [12]:

$$d = c(1-c)^{-\frac{1}{3}}\left(\frac{\rho}{\eta}\right)^{\frac{1}{3}}\omega^{-\frac{2}{3}}e^{\frac{1}{2}} \quad (2)$$

where ρ and η are the density and the viscosity of the solution, ω is the spin speed and *e* is the evaporation rate. If this formula is combined with Lambert-Beer law, the absorbance can be written as:

$$A = \varepsilon c^2(1-c)^{-\frac{1}{3}}\left(\frac{\rho}{\eta}\right)^{\frac{1}{3}}\omega^{-\frac{2}{3}}e^{\frac{1}{2}} \quad (3)$$

From this formula, absorbance varies exponentially with ω. The inset in Fig. 2 a) and b) show plots of the absorbance at 260 and 283 nm of the deposited FIBA and FIABA film versus the spinning speed, respectively. The exponential behaviour is shown in these graphs confirm the relationship described by Eq. 3. The relationship between absorption intensity and the solution concentration is plotted in the inset to Fig. 3 a) and b) for the FIBA and FIABA films, respectively. In these graphs, the absorbance increases linearly with the increase in the solution concentration. Our results are in good agreement with nickel 1,6,10,15,19,24,28,33-octa-*iso*-pentyloxy-2,3-naphthalocyanine complex thin film prepared by spin-coating method [25].

To determine the FIBA and FIABA thin film thickness, SE method was employed using a rotating compensator spectroscopic J. A. Woollam model M2000V instrument. The film thickness was evaluated from the experimentally measured spectra of the two ellipsometric parameters Ψ and Δ, representing the amplitude ratio and phase shift between *p*- and *s*- components of polarised light respectively. They are given as:

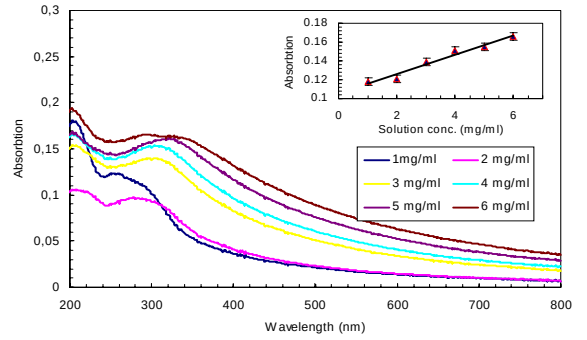
$$\Psi = \arctan\left(\frac{A_P}{A_S}\right) \quad (4)$$

$$\Delta = \varphi_P - \varphi_S \quad (5)$$

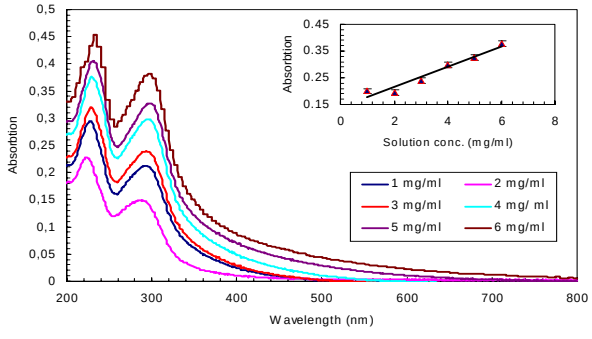
The procedure of fitting the experimental Ψ and Δ spectral values, consist of solving numerically the main ellipsometry equation given by [12]:

$$\tan(\Psi)e^{i\Delta} = \frac{\overline{R}_P}{\overline{R}_S} \quad (6)$$

where R_P and R_S are the Fresnel reflection coefficients for *p*- and *s*- components of polarised light. They are related to the optical parameters n, k and thickness d of the reflection system. These relations are expressed by Fresnel equations [26] and commercial software used for the fitting of the experimental data. Results of this fitting are given in Fig. 4.

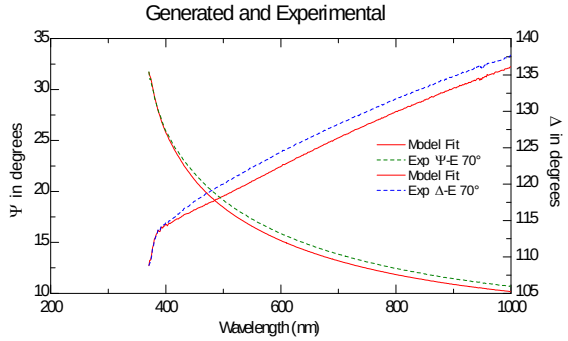


(a)

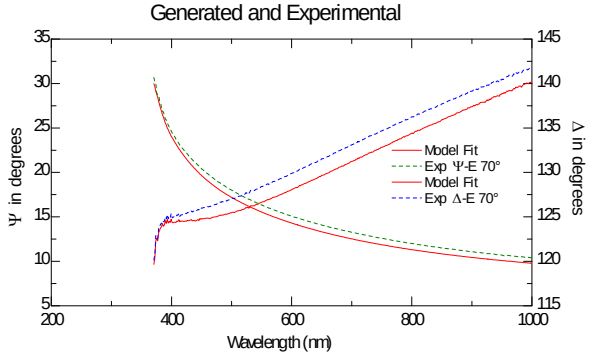


(b)

Fig. 3. UV-visible absorption spectra graphs of the (a) FIBA and (b) FIABA films obtained using different solution concentrations at 2000 rpm, spin speed.



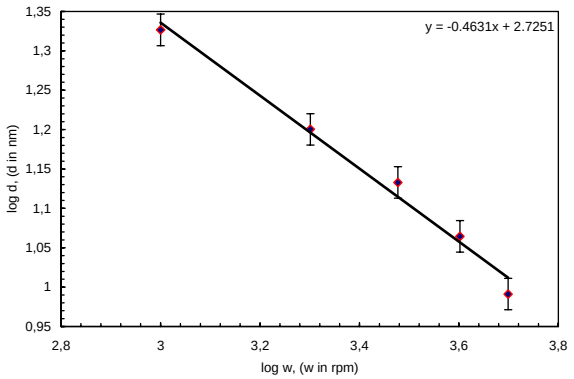
(a)



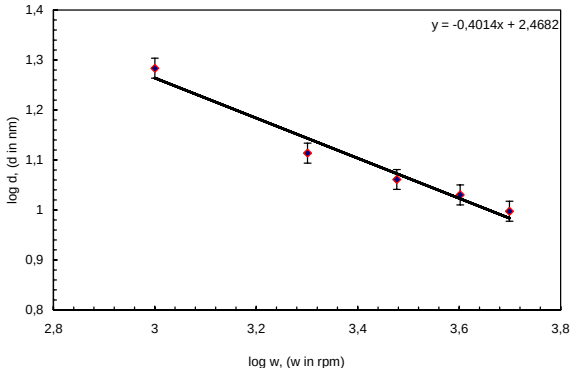
(b)

Fig. 4. Wavelength dependencies of, parameters Ψ and Δ at 2000 rpm spin speed for (a) FIBA and (b) FIABA thin films.

SE data was used to investigate the dependence of the film thickness on spin speed for samples prepared on silicon substrate in the spin range of 1000 rpm to 5000 rpm. Each silicon substrate was checked in order to determine the thickness of the silicon oxide layer, which was found to be about *2 nm*. Film thickness values at 2000 rpm are found to be *15.86 nm* and *d=12.99 nm* for FIBA and FIABA thin films. Fig. 5 gives the thicknesses of the FIBA and FIABA thin films as a function of spin speed. Using the comparatively less volatile organic solvents such as alcohols, film thickness dependence on spin speed is expected to follow the relation $d \sim \omega^{-0.5}$. In our work, the relation of film thickness is calculated to be $\omega^{-0.46}$ and $\omega^{-0.4}$ for the FIBA and FIABA films, respectively. These results are in a good agreement with the relation of $d \sim \omega^{-0.5}$ for the spin coated films [27-28]. It can therefore be established here that both novel phthalimide molecules studied here are suitable for thin film deposition by spin coating and can find potential application in thin film research area [29-31].



(a)



(b)

Fig. 5. Dependence of (a) FIBA and (b) FIABA film thickness as to the spin speeds.

4. Conclusion

Thin film properties of two novel phthalimide-based materials are studied using spin coating thin film method. UV-visible results for both materials showed $\pi \rightarrow \pi^*$ transition occurred in the B-band with a shift due to the polar ethanol solvent. Absorption spectra measured for thin films obtained from different solution concentration and absorbance increased linearly with the increase in the solution concentration. When the absorption of the FIBA and FIABA thin films were plotted against the spin speed showing exponential behaviour, film thickness dependence of the form $d \sim \omega^{-0.46}$ and $\omega^{-0.4}$ for the FIBA and FIABA films, respectively. The thicknesses of thin films at 2000 rpm are obtained 15.86 nm for FIBA and 12.99 nm for FIABA using spectroscopic ellipsometry results. Finally, both novel materials are a good candidate in the field of nanoscale thin film applications.

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