Spectroscopic ellipsometry investigation of the optical anisotropy in organic thin films

A. M. Paraian, G. Salvan, T. U. Kampen, M. Friedrich and D. R. T. Zahn
Institut für Physik, Technische Universität Chemnitz, D-09107 Chemnitz, Germany

Abstract. The optical properties of thin films of perylene derivatives grown on sulfur passivated GaAs(001) substrates were investigated *ex situ* in the energy range from 300 nm (4.13 eV) to 1700 nm (0.73 eV) by means of spectroscopic ellipsometry. In thin films of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) the molecules are aligned with their molecular plane parallel to the substrate surface. The in-plane refractive indices and extinction coefficients are found to be larger than the respective out-of-plane optical constants. In thin films of N,N`-dimethyl-3,4,9,10-perylenetetracarboxylic diimide (DiMe-PTCDI) the molecules are found to be oriented with the molecular plane tilted with respect to the substrate surface. For DiMe-PTCDI films of 20 nm the overall shape of the imaginary part of the dielectric function is very much alike with the absorption spectrum of DiMe-PTCDI film grown on quartz. One can easily identify the transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) at 2.16 eV. The imaginary part of the effective dielectric function shows a stronger dependence with the angle of incidence of the light compared to PTCDA. Together with symmetry considerations this proves a strong optical anisotropy of these organic films. As in the case of PTCDA films, the optical constants parallel to the molecular plane are found to be larger than the respective out-of-plane optical constants.

Keywords: organic thin films, PTCDA, DiMe-PTCDI, spectroscopic ellipsometry, optical anisotropy.

Corresponding author: Andreea M. Paraian
Institution: Technische Universität Chemnitz
Department: Institut für Physik
Address: D-09107 Chemnitz, Germany
Phone: ++49-371-531-3028
Fax: ++49-371-531-3060
E-mail: andreea.paraian@physik.tu-chemnitz.de

1. Introduction

Thin organic films of the archetype molecule 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) and N,N'-dimethyl-3,4,9,10-perylenetetracarboxylic diimide (DiMe-PTCDI) grown on passivated semiconductor substrates i.e. sulfur passivated GaAs are the subject of the present contribution.

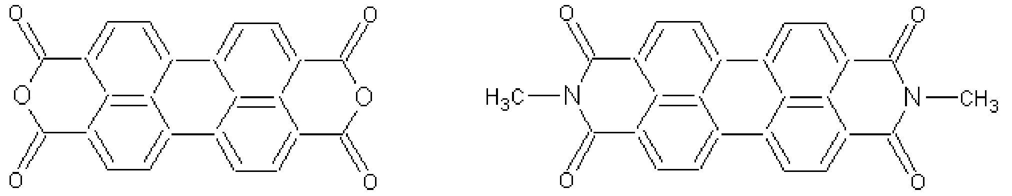
(a) (b)

Figure 1. The two perylene derivatives: (a) PTCDA and (b) DiMe-PTCDI.

Both organic materials crystallize in the monoclinic system with a C_{2h} symmetry having two molecules in the unit cell [1]. Due to their crystalline symmetry, anisotropy in the physical properties of these organic films is expected [2].

PTCDA has already been used as material for the deposition of films on various substrates ranging from van-der-Waals crystals [3] to metals such as Ag and Au [4] on which quasi-epitaxial growth is observed with the molecules lying almost flat and molecular plane being parallel to the substrate surface. It has recently been demonstrated that the growth of organic molecules on modified semiconductor substrates (e.g. Se-passivated GaAs(001) [5]) is considerably improved with respect to the growth on the corresponding bare substrate.

Adding the imide groups instead of the anhydride ones drastically modifies the growth mode of the organic film. It has been observed that for DiMe-PTCDI thin films grown on KCl surfaces the molecular planes are stacked parallel to the substrate [6] whereas the films grown on passivated semiconductor substrates have the molecular planes tilted with at an angle higher than 45° with respect to the substrate surface [7]. As it will be shown here the orientation of the organic crystallites has a deep impact on the optical properties of the films.

In this work spectroscopic ellipsometry is employed for the investigation of optical anisotropy of PTCDA and DiMe-PTCDI thin films grown on sulfur passivated GaAs and the advantages of generalized ellipsometry formalism are used for a quantitative analysis of the experimental results.

2. Experimental

All the samples being subject of this study were prepared using n-type GaAs(001) wafer pieces from Freiberger Compound Materials as substrate.

The first step in the sample preparation consists of degreasing the GaAs substrate using acetone, ethanol and de-ionized water in a ultrasonic bath for 5 minutes each followed by drying of the substrates in a dry nitrogen flux. The next step, the sulfur passivation, consists of dipping the substrates into a mixed solution of S_2Cl_2 and CCl_4 (1:3) for 10 seconds, the substrate is rinsed subsequently in CCl_4, acetone, ethanol and de-ionized water. The result of the sulfur treatment is a passivation of the surface with monolayer thick sulfides [8]. Immediately after the chemical treatment the substrates are transferred into the UHV system where annealing at 450°C takes place leading to a 2x1 reconstructed, sulfur terminated GaAs(001) surface, from now on referred to as S-GaAs(001). The organic material, i.e. PTCDA and DiMe-PTCDI purified by double thermal gradient sublimation is evaporated by means of Organic Molecular Beam Deposition onto the sulfur passivated substrates. During the organic material evaporation the substrates are kept at room temperature. The evaporation rate as monitored with the quartz microbalance was ~ 0.3 nm for both materials the resulting samples having thicknesses 120 nm for the PTCDA film and 20 nm, 120 nm respectively in the case of DiMe-PTCDI film.

The ellipsometry measurements were performed *ex situ* using a commercially available variable angle spectroscopic ellipsometer (WVASE® from J. A. Woollam Co., Inc.) equipped with vertical sample mounting stage, continuously rotating analyser, auto-retarder and a Xe lamp source. The vertical sample mounting stage is a high precision sample rotator allowing us to measure multiple azimuthal orientations. The angles of incidence of light used here are 20°, 45° and 70°.

The measured ellipsometric data are expressed in terms of the effective dielectric function[9]:

$$<\varepsilon>=\sin^2\Phi+\sin^2\Phi\tan^2\Phi\left[\frac{1-\rho}{1-\rho}\right]^2 \tag{1}$$

where $$\rho=\frac{r_p}{r_s}\tan(\Psi)e^{i\Delta} \tag{2}$$

is the complex reflectance ratio, Φ is the angle of incidence of light, Ψ and Δ are so-called ellipsometric angles, and r_p and r_s are the Fresnel coefficients for light polarized parallel and perpendicular to the plane of incidence, respectively.

2.1. Generalized ellipsometry

Generalized Ellipsometry (GE), introduced by Azzam and Bashara [10], is a very useful approach for characterization of the optical and structural properties of anisotropic layered materials. This technique provides normalized Jones reflection matrix elements, which in the case of an anisotropic system can be expresed as:

$$\begin{pmatrix} E_r^p \\ E_r^s \end{pmatrix}=\begin{pmatrix} r_{pp} & r_{ps} \\ r_{sp} & r_{ss} \end{pmatrix}\cdot\begin{pmatrix} E_i^p \\ E_i^s \end{pmatrix} \tag{3}$$

where i and r indices refer to the light incident onto and reflected from the sample, respectively. For isotropic materials the off-diagonal terms vanish and the relationship between $\Psi$and Δ and the material dielectric function is given by equation (2). In general however, incident and reflected polarization states are related by the following expressions:

$$\begin{aligned} &\frac{r_{pp}}{r_{ss}}=\tan(\Psi_{pp})e^{i\Delta_{pp}}, \\ &\frac{r_{ps}}{r_{pp}}=\tan(\Psi_{ps})e^{i\Delta_{ps}}, \\ &\frac{r_{sp}}{r_{ss}}=\tan(\Psi_{sp})e^{i\Delta_{sp}} \end{aligned} \tag{4}$$

For optical investigations on anisotropic samples it is necessary to specify the in-plane orientation of the sample with respect to the plane of incidence which is done using the Euler angle formalism. The Euler angles (φ, θ and ψ) used by the WVASE package [11] correspond to rotations arounf the z-axis, then around the new x-axis, and then again around the new z-axis.

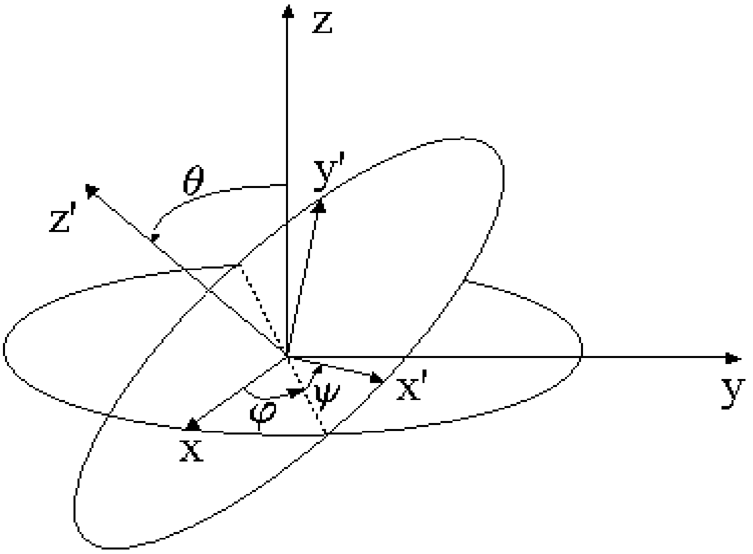

Figure 2. Definition of the Euler angles φ, θ and ψ; (x', y', z') and (x, y, z) refer to the organic films' axes, and substrate coordinate systems, respectively.

3. Results and discussion

The anisotropic optical behaviour of thin films of PTCDA grown on sulfur passivated GaAs(001) was thoroughly discussed elsewhere [12, 13]. Here evidence for the optical anisotropy of such films is provided by new results obtained with the help of generalized ellipsometry measurements. The left-hand side panel of fig. 3 shows the results of an generalized ellipsometry scan of a 120 nm thick PTCDA film at an angle of incidence of light equal to 70°. As mentioned in the subsection above the measured values are not longer expressed in terms of the equation (2) but rather by the more complicated relations (eq. (3)). One can clearly observe that the change of state of polarization from p to s (Ψ_{ps}) and also from s to p (Ψ_{sp}) gives quite an important contribution to the measured spectrum thus giving strong evidence for the anisotropic character since for an isotropic material one should expect null values for Ψ_{ps} and Ψ_{sp}. In the right-hand side panel the imaginary part of the effective dielectic function for the same angle of incidence, 70°, as a function of the sample azimuthal orientation is shown. Here, 0° and 90° signifies that the plane of incidence contains [110] and [-110] directions of the substrate, respectively, and 45° means an azimuthal orientation of the sample such that the plane of incidence makes a 45° angle with any of the substrate axes. Although the azimuthal dependence of Im<ε> is not very well visible the in-plane optical anisotropy of PTCDA films deposited on sulfur passivated GaAs substrates is supported also by reflectance anisotropy spectroscopy results [13].

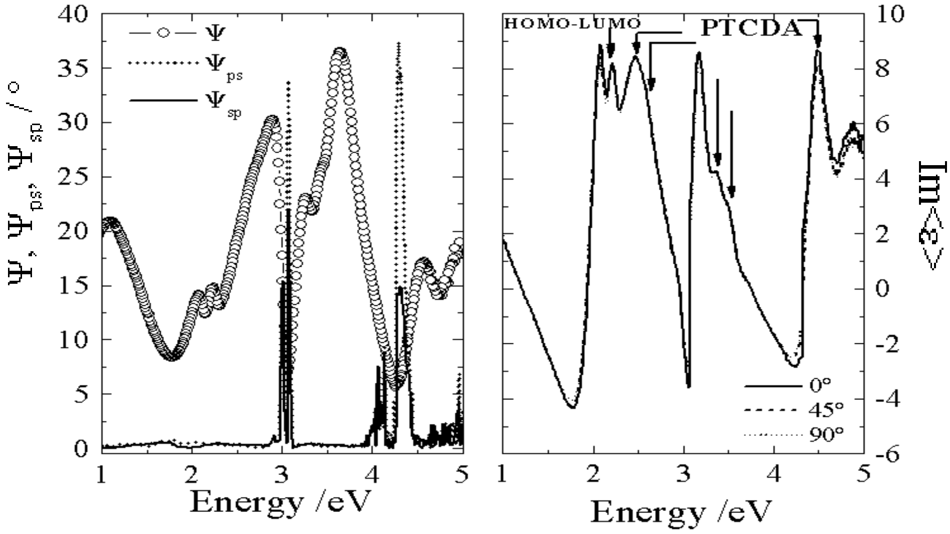

Figure.3. Results of generalized ellipsometry measurements of 120 nm PTCDA film grown on S-GaAs(001) substrate.

For thin films of DiMe-PTCDI the overall shape of the imaginary part of the dielectric function is very similar with the absorption spectrum of a DiMe-PTCDI film grown on quartz as it can be seen in fig. 4. Energy positions of the optical transitions were determined by curve fitting of the absorption spectrum. In the spectrum of imaginary part of the effective dielectric function the optical transitions of DiMe-PTCDI are very well resolved such as the transition from the highest unoccupied molecular orbital (HOMO) to the lowest occupied molecular orbital (LUMO) located around 2.16 eV. The higher observed transitions are also in a very good agreement with those in the absorption spectrum marked by dashed-dotted line. Figure 5 shows the azimuthal dependence of Im<ε> for a 120 nm DiMe-PTCDI film which compared to the case of PTCDA has changed dramatically.

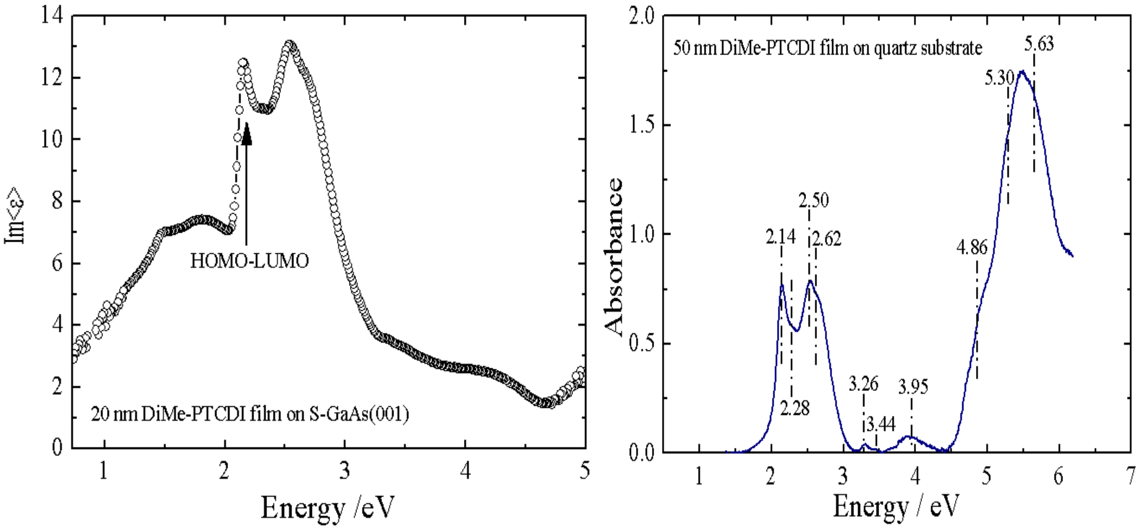

Figure 4. Imaginary part of the effective dielectric function for a 20 nm DiMe-PTCDI film on sulfur passivated GaAs(001) (left) and absorption spectrum of 50 nm DiMe-PTCDI film grown on quartz substrate (right).

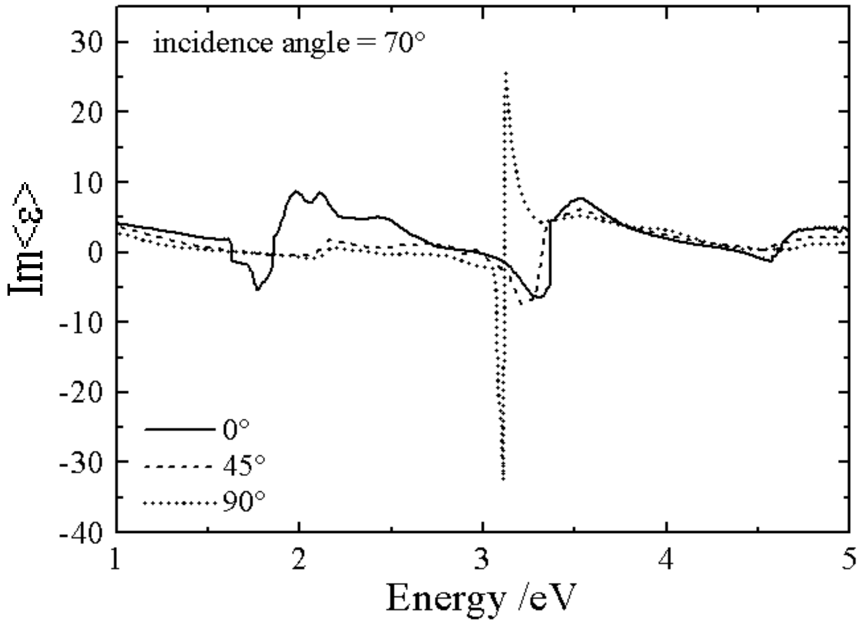

Figure 5. Azimuthal dependence of Im<ε> for 120nm DiMe-PTCDI film on S-GaAs(001); 0°, 45° and 90° (legend) are the same as in fig. 3.

When the plane of incidence contains the [-110] direction of the substrate the imaginary part of the dielectric function is dominated by a strong feature around 3.1 eV. This feature can be attributed to $E_1+\Delta_1$ critical point of GaAs and it is strong enhanced due to interference effects.

For quantitative analysis of the generalized ellipsometry results for thicker (~120 nm) DiMe-PTCDI films a fitting procedure was constructed as follows: a GaAs layer with tabulated optical constants was used as substrate while for describing the DiMe-PTCDI layer a so-called *biaxial layer* was employed taking into consideration the anisotropic nature of the organic layer. This means that different optical constants with respect to all three cartesian axes are considered, along with the orientation of the optical axis of the film which is described by the tilting angle θ in respect to the z axes (normal to the film plane). In the spectral region below 2 eV, where the organic film is transparent, the dispersion of the refractive indices along the x, y and z directions was described by a Cauchy relation and a fit was performed for determining the layer thickness, θ angle and the Cauchy parameters. The fit results are 122 nm ± 1 nm for the layer thickness and 51°±2° for θ. The value obtained for the θ angle is in good agreement with those obtained from the analysis of infrared and NEXAFS spectra which clearly show that the orientation of the molecules with respect to the substrate surface is neither parallel nor perpendicular to the GaAs surface.

The optical constants of the organic film along the x, y and z directions over the entire measured spectral region are described by oscillators (Gaussians) having energy positions corresponding to the optical transition energies observed in the absorption spectrum. The obtained optical constants are displayed in fig. 6 (a) and (b).

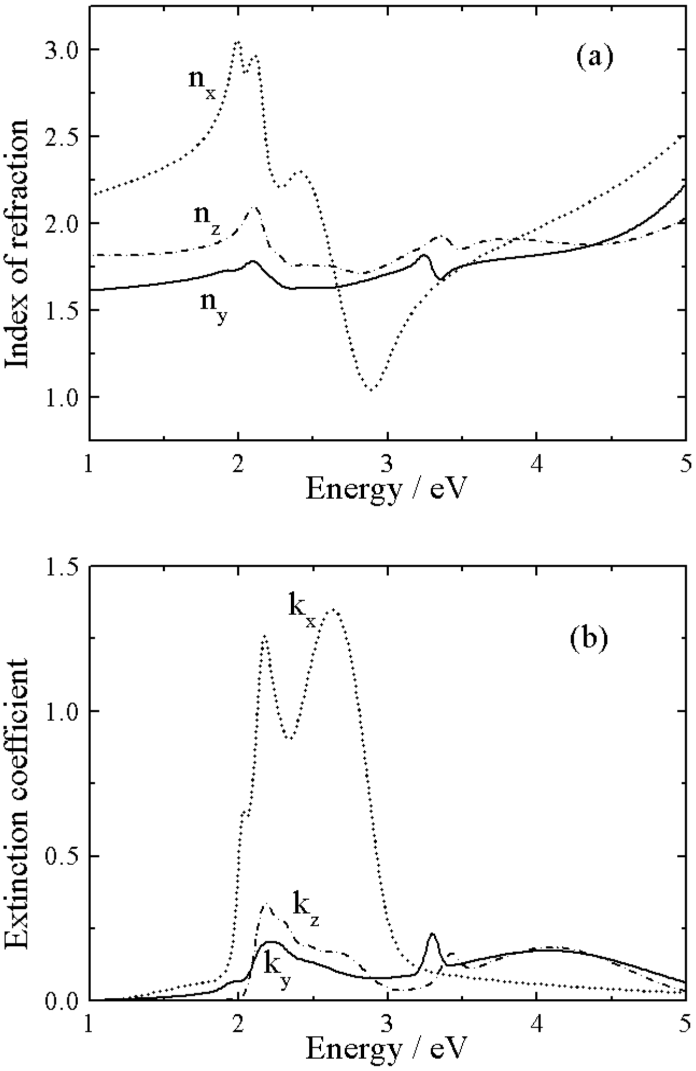

Figure 6. Refractive index (a) and extinction coefficient (b) of DiMe-PTCDI film as determined by fitting the generalized ellipsometry data.

4. Conclusion

Dramatic changes are observed in the ellipsometry spectra when comparing thin films of two perylene derivatives i.e. PTCDA and DiMe-PTCDI. The former is known to lie almost flat with respect to the substrate (GaAs) whereas the later is proved to have an tilt angle with respect to the substrate surface when the films are grown on S-GaAs(001) substrates. The orientation of the optical axis for the DiMe-PTCDI film has been determined by fitting the ellipsometry data and the obtained value is in agreement with the results obtained by other optical and electron spectroscopy techniques.

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