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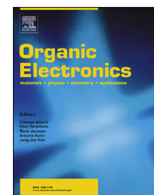

Determination of crystal orientation in organic thin films using optical microscopy

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ABSTRACT

The electrical behavior of devices based on highly crystalline thin films of organic semiconductors is inherently anisotropic. Thin film optimization requires simple and accessible means to characterize the orientation of the constituent crystals. The standard polarized light microscopy (PLM) provides a contrast between different crystallites but fails to distinguish crystals with relative orientation of 90°. In this paper, we discuss two methods that enable the unambiguous identification of crystal orientation in thin films of optically anisotropic materials: PLM with a full-wave retardation plate and differential interference contrast (DIC). The latter is standard on most microscopes and delivers images with high contrast and good color balance.

As an illustration, we use DIC to extract the optical properties of highly crystalline thin films of three high-performance organic semiconductors: rubrene, 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene) and 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C_8-BTBT). Building on the relation between optical properties and crystal orientation, we demonstrate how DIC characterizes the in-plane crystal orientation of these thin films. This leads to the identification of the fast growth direction of the crystal front.

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1. Introduction

Organic semiconductors are an important class of materials that can be processed at low temperatures on plastic foils and thus enable low-cost [1,2], flexible electronic applications [3–7]. In recent years, optoelectronic devices based on single crystalline organic thin films gained popularity thanks to their high performance [8–11]. The electrical properties of most organic single crystals are, however, highly anisotropic [12–14]. Hence, if thin-film devices are built on separate crystallites with different orientations, the anisotropy will result in undesirable device-to-device variation. In order to minimize this spread and understand crystal growth, one requires a characterization technique that can determine crystal orientation.

Polarized light microscopy (PLM) is by far the most popular optical technique for imaging highly-crystalline organic thin films [15,16]. The advantages of PLM are good contrast between different crystal orientations, fast image acquisition, submicrometer lateral resolution and large field of view. In PLM an optically anisotropic crystal has maximum brightness when its slow or fast axis is at 45° to the polarization of incident light [17]. Since both slow and fast axes result in equivalent brightness, the crystal orientation cannot be unambiguously identified.

In this paper we explain how two microscopy methods can lift this ambiguity: the use of a full-wave retardation plate in the light path of PLM and, alternatively, the use of another standard optical technique, differential interference contrast (DIC). The latter is superior as it requires only standard microscopy components and delivers images with high contrast and good color balance. In the methods section, we first explain the relationship between optical and structural properties of anisotropic materials and then describe in detail the principles of PLM, PLM with a full-wave plate and DIC. Next, in the results section, we characterize highly crystalline thin films of some popular high-performance organic semiconductors. We show how the slow and fast axes can be found with both

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methods and demonstrate the unambiguous identification of in-plane crystal orientation in these thin films.

2. Microscopy methods

2.1. Optical and structural properties of thin films

Optical properties of an anisotropic material are defined by its index ellipsoid [18]. The radii of the ellipsoid indicate the refractive indices for the incident light polarized along the radii directions. In an optical microscope, the polarization direction of incident light is restricted to the plane of the microscope stage. Then, the optical properties of the crystalline thin film are defined by the cross-section of this plane and the index ellipsoid of the crystal. The obtained cross-section gives an index ellipse. Minor and major axes of this ellipse, called fast and slow axes, yield refractive indices n_1 and n_2 ($n_2 > n_1$) for the incident light polarized along these axes.

For a certain wavelength, the orientation of the index ellipsoid relative to the crystallographic axes of the crystal is fixed. It is decided by susceptibility of the electronic configuration to distortion inside the crystal [18]. In organic materials, this susceptibility depends both on the molecular structure and the polymorph considered [19]. Theoretical methods such as density functional theory (DFT) calculations can be used to calculate this relationship, but they are expensive considering the wide variety of possible systems [20]. If studied thin films form epitaxial layers such as having one crystal axis somewhat aligned with the normal to the substrate, the problem simplifies to finding the relationship between the index ellipse and the in-plane crystal orientation. In case of single crystalline epitaxial films, the index ellipse can be found experimentally using, for example, ellipsometry [19] or polarized absorption spectroscopy [21] while the crystal orientation – using the crystal shape [22] or x-ray diffraction (XRD) measurements [16]. In our work, we find optical properties using light microscopy techniques while the in-plane crystal orientation is obtained from preferential crystal cracking directions.

2.2. Polarized light microscopy

PLM is a simple optical technique for imaging thin films with different crystal orientations. It requires two linear polarizers in the light path that have mutually crossed polarization directions. First, unpolarized light of the light source gets linearly polarized in the East-West direction by the first polarizer (Fig. 1). It illuminates the optically anisotropic crystal that has the refractive indices n_1 for the fast axis and n_2 – for the slow axis.

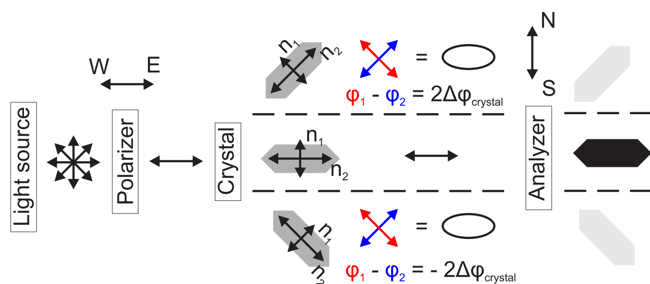

Fig. 1. Schematics of light propagation in an anisotropic crystal during PLM in reflected configuration. The fast and slow axes of the crystal have refractive indices n_1 and n_2 respectively. When the fast or slow axes of the crystal n_1, n_2 are parallel to the polarizer, the crystal appears dark (middle row). When the slow axis of the crystal n_2 is at 45° or 135° to the polarizer, the crystal have equivalent maximum brightness (top and bottom rows) that prevents unambiguous identification of fast and slow axes. The color of the crystal is defined by the retardation of the reflected beams $\Gamma = \varphi_1 - \varphi_2$ according to the Michel-Lévy chart.

While passing through the crystal, the incident light does not change its properties as long as the polarization of the beam is parallel to the fast or slow axes (middle row in Fig. 1). In the reflection configuration the light is reflected either from the substrate or the glass plate underneath (in case of transparent substrates) and is directed to the second polarizer (analyzer). Since the analyzer has the North-South polarization, the reflected beam is blocked due to its orthogonal polarization and the crystal appears dark (extinction).

Alternatively, when the polarization of the incident light does not coincide with the fast or slow axes of the crystal, the beam polarization is projected on them, thus producing two beams polarized along these axes (birefringence) (top and bottom rows in Fig. 1). As these beams experience different refractive indices, they will propagate in the crystal with different speeds and acquire a relative phase delay (retardation) $\Gamma = \varphi_1 - \varphi_2 = 2t(n_1 - n_2) = 2\Delta\varphi_{crystal}$ or $-2\Delta\varphi_{crystal}$ if the slow axis of the crystal is at 45° or 135° to the polarizer. The thickness of the crystal t is accounted twice because the beam passes the crystal twice in the reflected configuration. The superposition of these retarded beams gives elliptically polarized light. When it reaches the analyzer, polarizations of its constituting components are projected on the analyzer and resulting beams interfere with each other. The crystal appears bright and its maximum brightness is observed when the components of the elliptically polarized light have the largest total projection of their polarizations on the analyzer. This happens when the slow axis of the crystal n_2 is either at 45° or 135° to the polarizer (top and bottom rows in Fig. 1). Since both cases have equivalent brightness, the direction of fast and slow axes cannot be unambiguously identified.

Additionally, the color change of the crystals is observed when illuminating them with polarized white light. If the retardation Γ is equal to the particular wavelength, the two beams of this wavelength leave the crystal as if there was no retardation and result in the same linearly polarized light as the one that entered the crystal. Consequently, this wavelength does not pass the analyzer and the color of the crystal changes according to the Michel-Lévy interference color chart [23]. Since only the absolute value but not the sign of the retardation Γ influences the color change, crystals with retardations $2\Delta\varphi_{crystal}$ and $-2\Delta\varphi_{crystal}$ will have the same colors (Fig. 1, top and bottom cases).

To lift this ambiguity, additional retardation plates or compensators are required in the light path, e.g. a full-wave retardation plate, a de Senarmont compensator, a Brace-Köhler compensator, etc. [18] For example, Fig. 2 depicts light propagation of polarized light with a full-wave plate. Typically the plate with retardation $\Delta\varphi_{plate} = 530$ nm (full wavelength for green light) is inserted after the polarizer and before the analyzer. The angle between the slow axis γ of the full-wave plate and the polarizer should be 45°. The incident linearly polarized beam is decomposed in two orthogonal beams that acquire retardation of $\Delta\varphi_{plate}$ after passing through the full-wave plate. While traversing the anisotropic crystal, the beams gain an additional retardation $2\Delta\varphi_{crystal}$ or $-2\Delta\varphi_{crystal}$ if the slow axis of the crystal n_2 is parallel or perpendicular to the slow axis γ of the plate (top and bottom rows in Fig. 2). If the slow or fast axes of the crystal n_1, n_2 are parallel to the polarizer, the beams do not get additional retardation (middle row in Fig. 2). Reflected beams pass again the full-wave plate that adds retardation $\Delta\varphi_{plate}$ to their total phase delay. In all three cases the reflected beam is elliptically polarized and can cross the analyzer. According to the Michel-Lévy chart, the color of the crystal changes from dark purple to light purple for thin crystals with the retardation $\Delta\varphi_{crystal}$ much smaller than $\Delta\varphi_{plate}$. Thus, fast and slow axes of the crystal n_1, n_2 can be unambiguously identified from the crystal color change. The

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