Mapping chemical concentration in binary thin organic films via multi-wavelength scanning absorption microscopy (MWSAM)

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Abstract
The composition and thickness of binary thin organic films is determined by measuring the optical absorption at multiple wavelengths across the film surface and performing a component analysis fit to absorption standards for the materials. The multiple laser wavelengths are focused onto the surface using microscope objectives and raster scanned across the film surface using a piezo-electric actuator X–Y stage. All of the wavelengths are scanned simultaneously with a frequency division multiplexing system used to separate the individual wavelength response. The composition values are in good quantitative agreement with measurements obtained by scanning transmission x-ray microscopy (STXM). This new characterization technique extends quantitative compositional mapping of thin films to thickness regimes beyond that accessible by STXM.

Keywords: organic solar cells, thin film analysis, composition mapping, optical absorption spectroscopy

(Some figures may appear in colour only in the online journal)
STXM is capable of achieving chemical contrast due to the differences in the x-ray absorption spectra of the component materials. Based upon this principle, NEXAFS has been used to compositionally map P3HT:PCBM blend films with a lateral spatial resolution below 100 nm [13–15]. However, STXM has two key limitations. Firstly, STXM is limited in its use to thin films since the signal strength drops below detectable levels when the film thickness exceeds ~100 nm. Secondly, STXM requires a synchrotron radiation source to generate the required intense monochromatic x-ray beams.

Here we report the development of a new multi-wavelength scanning absorption microscopy (MWSAM) technique, which is an optical analogue of STXM, and is capable of generating a vertically averaged compositional map of an organic thin film with a resolution of around 1 µm whilst simultaneously providing a measure of the film thickness. As a case study, this new MWSAM system is used to map micrometre scale phase segregation in the P3HT:PCBM system and we show that it yields quantitative information about the fractional composition of the binary organic films that is in good agreement with our previous STXM studies. Finally, we show that the new technique is capable of measuring the composition of much thicker features than hitherto possible using STXM.

2. Experimental

2.1. Equipment configuration

The new SAM technique combines component analysis and optical absorption spectroscopy over areas of a few square micrometres to determine the thickness and composition of an organic thin film. The system was built onto an existing microscope set-up which acts as a framework to hold all of the optics in place. An achromatic microscope objective is used to focus the probe light onto the surface of the film under study.

The multi-wavelength probe light is generated by an array of lasers mounted on an optical bread board. Each wavelength is modulated by an optical beam chopper at a unique frequency before being combined into a single beam and coupled into a single mode polarization maintaining fibre. The output of the fibre is collimated using an off-axis parabolic reflective collimator which is located at the top port of the trinocular microscope. The light passes through a beam splitter, which, together with a photodiode monitors the intensity of the input light. The probe light is then focused onto the film under investigation with a photodiode monitors the intensity of the input light. The probe light is then focused onto the film under investigation with a photodiode monitors the intensity of the input light. The probe light is then focused onto the film under investigation with a photodiode monitors the intensity of the input light. The probe light is then focused onto the film under investigation with a photodiode monitors the intensity of the input light. The probe light is then focused onto the film under investigation with a photodiode monitors the intensity of the input light. The probe light is then focused onto the film under investigation with a photodiode monitors the intensity of the input light. The probe light is then focused onto the film under investigation with a photodiode monitors the intensity of the input light.

A multiplexer (Demux) is used to select the required wavelength for the experiment. The system also includes a reflective collimator and a photodiode to detect the transmitted light. The transmitted light is then focused onto a photodiode using an achromatic microscope objective.

2.2. Light measurement

In order to produce chemical compositional information, the absorption of the probing light by the film needs to be performed at multiple wavelengths either sequentially or simultaneously. A simple way to avoid the complexity of multiple sequential scans is to use a frequency division multiplexing (FDM) technique to differentiate each wavelength using only a photodiode. The technique has been discussed in detail elsewhere [17] and will only be described briefly here for clarity. To perform the FDM, each probe wavelength is modulated at a unique frequency which is not a harmonic of any of the other frequencies. The modulated light then excites the photodiodes to produce a voltage signal which is proportional to the intensity of the wavelength at the modulation frequency of that wavelength. The intensity of each wavelength is then recovered by using the Welch technique for estimation of the periodogram on the voltage–time series from the diode. A 50% overlap in the window is used for the signal recovery. The light intensity is measured at both the input photodiode and the transmitted-light diode.
To determine the incident light intensity on the film, the probe wavelengths are transmitted through a section of substrate not covered by the film, which enables determination of a ratio between the signal from the monitor-diode and the actual incident light intensity measured by the transmitted-light photodiode.

2.3. Calibration standards

To perform the analysis necessary to determine the film composition and thickness it is necessary to know how the absorption varies with the blend ratio in the film. To establish this relationship, calibration standards of known composition are created by spin coating a series of films with varying blend ratios onto glass substrates. For the P3HT : PCBM test sample presented in section 3.2, the blend ratio between the two materials was varied from 1 : 10 to 10 : 1 to cover most possible blend ratios. By creating this set of calibration standards, no assumption is made about the blend absorption spectra being simple linear combinations of the pure materials absorption spectra.

While it is important that all the calibration films are of the same average thickness, it is not necessary to measure the individual thickness of each of the calibration films. Instead, it is possible to compare film thicknesses of materials with varying blend ratios by considering the isosbestic point in the UV–vis absorption curve. If the isosbestic point is invariant for all blend ratios then the films are necessarily of the same thickness, even if the specific thickness is not known. A common isosbestic point for the examined P3HT : PCBM system can be seen in figure 3(a) at ~433 nm.

2.4. Component analysis

Component analysis is used to determine the composition and thickness of the film at each point of the scan. The analysis makes use of the absorption spectra of the calibration standards. The absorption at the probe wavelengths is plotted against the relative concentration of one of the constituent materials as in figure 3(b). A second order polynomial is then fitted to each data series to provide a smooth interpolation between the data points. It is sufficient to use a second order polynomial, as for a given wavelength the absorption will either be monotonically increasing or decreasing with concentration. The calibration fit for the i\textsuperscript{th} wavelength can then be written as $A_i = a_1 C^2 + a_2 C + a_3$, where $a_1$, $a_2$, $a_3$, and $C$ are the coefficients of the fitted polynomial and $C$ is the concentration.

The calibration equations can then be used to find the concentration $C$ and thickness $T$ of a film at any point by measuring the absorption $A_i$ at multiple wavelengths ($i$) and finding $T$ and $C$ which minimize the expression: $\sum_{i=1}^{n} [A_i - TA_i(C)]^2$.

The $T$ value found from this fit is the optical thickness of the film, and is relative to the thickness of the calibration standard films. The $C$ value is the concentration found as a ratio of the constituent material used in the calibration.

For multicomponent blend films an identical analysis may be performed to determine the concentration of each component as long as the sample is probed with at least as many wavelengths as there are components in the system.

3. Characterizing the SAM system

3.1. Resolution

In order to determine the resolution of the instrument, a test sample of well-defined shape and size was created and analysed. The sample chosen was a 1 µm hole which had been milled into a 300 nm thick gold–hafnium alloy foil. The resolution of the instrument was determined by scanning over the 1 µm pinhole whilst measuring the transmitted light intensity. Since the foil is perfectly opaque, and the edges of the hole are near perfectly sharp the resolution of the instrument could be determined by the distance taken for the transmitted light intensity to reach a maximum. The transmitted light images of the pinhole (one for each of the wavelengths) were normalized to the maximum value in each image. Profiles through the centre of each image were then examined and the resolution defined to be the distance over which the profile goes from 20% of the maximum value to 80% of the maximum value.

The profiles of the pinhole images (figure 2) show that the resolution of the instrument is dependent on the wavelength of the light employed in accordance with the Rayleigh criteria. Since we are using multiple wavelengths, the final resolution will be limited by the spot size of the longest wavelength used. The resolution systematically broadens with increasing wavelength and is 1.2 µm for the 405 nm spot, 1.4 µm for the 532 nm light and 1.5 µm for the 660 nm light.

3.2. Case study

The technique was demonstrated using the well-studied [16] P3HT : PCBM thin film, the active layer blend utilized in many bulk heterojunction organic solar cells. This system...
was used as a case study as it is currently the most studied OPV system and because of the known tendency for the constituent component materials to phase segregate upon thermal annealing [15, 18].

The sample was prepared by dissolving P3HT and PCBM in chloroform (CHCl 3) in a ratio of 1:1 and a concentration of 25 g l−1. The film is then spin coated onto a glass substrate to produce a film which is ~120 nm thick. The film was thermally annealed at 140 °C for 40 min on a hotplate and placed onto an insulating material to cool, resulting in a highly phase segregated film, with the PCBM forming large aggregates within the blended matrix.

The film was then placed under the microscope and an absorption scan was performed. The optical thickness and composition maps were then generated using the calibration standards as outlined above.

3.3. Wavelength selection and calibration

The selection of the wavelengths used was dictated by the absorption spectra of the component materials, the optics in the system and available wavelengths of laser sources. In order to achieve greater sensitivity, it is useful to select wavelengths which have increasing absorption for each of the materials in the blend. In figure 3, it can be seen that 405 nm light (to the left of the isosbestic point) has increasing absorption with increasing PCBM concentration, while the 532 nm light (to the right of the isosbestic point) shows increasing absorption with increasing P3HT concentration. By contrast, the 660 nm light does not show any real chemical sensitivity as the absorption is invariant with concentration. In addition to the lack of chemical sensitivity, 660 nm light limits the system resolution to 1.5 μm (figure 2) and hence is not a suitable wavelength for this material system. Based on the UV–vis absorption spectra presented in figure 3(a), greater PCBM sensitivity would be achieved by selecting a wavelength shorter than 405 nm. Such a wavelength would result in a steeper curve (figure 3(b)) but would be incompatible with the current optics.

4. Results and discussion

Figure 4 shows a typical SAM scan of the P3HT:PCBM film, highlighting the presence of a PCBM aggregate. The optical thickness map generated by this scan shows that the bulk film is ~1.5 times the thickness of the standard film; corresponding to a thickness of ~120 nm. The aggregate shows up as a protrusion on the surface, surrounded by a depression or depletion zone in the bulk film. By comparing these regions with the corresponding regions in the composition map, it is apparent that the aggregate is composed primarily of PCBM and that the depression surrounding it is depleted of PCBM and is rich in P3HT. This observation is consistent with previous studies using STXM to determine film and aggregate composition [15]. By contrast, the bulk film has a concentration of ~50% PCBM, which compares favourably with the prepared blend ratio.

Figure 3. (a) UV–vis absorption for P3HT:PCBM ratios of 10:1 (dotted line), 2:1 (solid line) and 1:10 (dashed line), along with the selected probe wavelengths. The variation in absorption for each wavelength with P3HT concentration is shown in (b) for all of the calibration films along with the polynomial fits (solid lines) used in the analysis. The standard fractional error in the UV–vis measurement is ±0.05 [19].

To more directly compare the optical thickness map with the composition map, line scans were taken through the centre of the aggregate. In figure 5(a) the profile of the optical thickness map is plotted along with the average value for the profile. Since the average value is equal to the value for the optical thickness in the bulk (far from the aggregate), this indicates that all of the material lost from the depletion region around the aggregate has gone into the aggregate and thus all of the material is accounted for.

The profile of the composition map (figure 5(b)) shows that the aggregate region is ~70% PCBM, whilst the depletion region surrounding the aggregate is only ~20% PCBM. Watts et al reported very similar results for the concentration profile from the edge of the aggregate outwards into the bulk film [15]. Their STXM measurements show that the composition of the film in the depletion region immediately surrounding the aggregate was ~20% PCBM. Furthermore, the concentration increases back to the blend ratio (for their 52.5% blend) over a distance of about 5 μm. The profile shown in figure 5(b), obtained using the scanning optical absorption technique matches this STXM profile over this region of the film.

Composition measurements directly over the aggregate were not possible in the STXM investigation due to the high optical density in this region [15]. However, in the case of SAM, composition measurements are possible over the aggregate and the optical absorption data presented here show that
the concentration of the film in the aggregate region is around 70% PCBM. Since the optical absorption produces a vertically averaged composition, it is uncertain whether the P3HT is present as a wetting layer, a capping layer or both. However, previous ellipsometry [20] and x-ray scattering [12] studies indicate that the P3HT forms a wetting layer beneath the PCBM aggregate upon thermal annealing.

In summary, we have successfully demonstrated a multi-wavelength scanning absorption microscope capable of determining the composition and thickness of thin binary organic films with a resolution of ~1 µm. While the technique does not provide depth resolution, it does provide a simple, bench top method for mapping the chemical composition of thin films which compares favourably with other available methods.

5. Conclusion

We have developed a scanning microscopy technique capable of measuring the composition and thickness of a thin film using optical absorption spectroscopy. The resolution of the system was determined to be around 1.4 µm using a pinhole in a gold-alloy foil and is directly determined by the wavelength of the probe. The chemical composition and thickness mapping was demonstrated using a P3HT:PCBM thin (~120 nm) film. The results show that the PCBM forms aggregates in the film, leaving the film depleted of PCBM in the immediate surroundings of the resulting aggregate. The concentration of PCBM returned to the bulk blend ratio over a distance of around 5 µm, in agreement with previous STXM results. It was also shown that the optical absorption mapping was capable of determining the composition on substantially thicker films than is possible with the STXM.

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