# Probing organic nanostructures by photoelectron-emission microscopy

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A B S T R A C T

Photoelectron-emission microscopy (PEEM) is a very versatile tool for studying dynamic processes like growth and phase transitions on surfaces. Here we have applied PEEM to the growth of $\alpha$-sexithiophene ($\alpha$-6T) on Ag(1 1 0) surfaces to study the formation of the wetting layer and the initial stage of 3D growth. In this paper we want to point out how different light sources available in the lab can be used to obtain complementary information. We will also discuss the use of linear polarized light (Hg lamp) in this context.

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## 1. Introduction

The fundamentals of the photoelectron-emission microscopy (PEEM) technique were described in the literature already in the early 1930's [1,2]. A bright light source, usually a mercury arc discharge lamp (Hg lamp), excites photoelectrons from the sample surface. The lateral variation of the work function or the ionization potential as well as field enhancement due to the topography of the sample contribute to the contrast in PEEM [3]. Besides the good lateral resolution down to some 10 nm, PEEM allows studying processes like growth and phase transitions with near video rate temporal resolution. In fact, the response is often just limited by the fluorescence life time of the phosphorous screen used for the electron detection. Using pump probe techniques, plasmon dynamics can be studied at a time scale below one femto second [4–6]. In this paper, we will focus on standard light sources (Hg, $D_2$, and He lamps) and how they can be used to study the growth of $\alpha$-sexithiophene ($\alpha$-6T) on Ag(1 1 0) surfaces in real-time.

## 2. Material and methods

For the experiments described, we used a Ag(1 1 0) single crystal (Mateck GmbH) with a nominal surface miscut of less than 0.1°. To clean the surface, repeated cycles of $Ar^+$ ion sputtering (0.9 kV, 3.6 $\mu A/cm^2$ for 60 min) and subsequent annealing at 600 K were applied until no impurities could be detected by Auger electron spectroscopy.

The commercially available $\alpha$-sexithiophene was purified by gradient sublimation before inserting it into a Ta-crucible. The $\alpha$-6T films were prepared within the PEEM setup while monitoring the intensity integrated over the whole image. If a Hg lamp is used for the excitation, the global maximum of the intensity can be identified with the completion of the monolayer – similar to the case of p-6P on Cu(1 1 0) – (2×1)O [7] or pentacene on Si(0 0 1) [8].

The experiments were carried out in an ultra high vacuum system (base pressure below $5\times10^{-10}$ mbar) housing a Focus IS-PEEM with a retarding field energy analyzer [9]. The PEEM is equipped with an integrated sample stage whose high mechanical stability allows a lateral resolution of about 50 nm. The actual lateral resolution of the PEEM images shown in Fig.3 is lower due to pixel resolution of the CCD camera and the difficulty to adjust the focus correctly before the growth experiment. It can be estimated to be about 150 nm.

The light of the standard Hg lamp (4.9 eV, Focus GmbH) can be linearly polarized by using a calcite Glan–Thomson prism (B. Halle GmbH). On the same port a $D_2$ lamp (Hamamatsu Photonics) can be mounted, which is purged with nitrogen gas to reduce absorption by the ambient air. Due to the optical port of the vacuum system and the in vacuo lens the spectrum of the deuterium lamp is limited to a photon energy of approximately 6.4 eV. Another port is used to mount a differentially pumped Helium discharge lamp (Focus HIS 13, 21.2 eV). For all excitation sources, the angle of incidence of the light beam with respect to the surface normal is about 65°.

The emitted photoelectrons are imaged by an electrostatic lens system onto a fluorescence screen. The images are acquired with a 12 bit CCD camera (PCO AG, Pixelfly). Usually the double multi-channel-plate is sufficient to achieve a good signal to noise ratio for an exposure time of 700 ms. If needed the noise can be reduced by averaging over several images.

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## 3. Results and discussion

Fig. 1 shows PEEM snapshots of an area with a diameter of ~35 μm. On this Ag(1 1 0) surface about 6 ML of α-6T were deposited while the substrate was held at 334 K. If the coverage of α-6T on a Ag(1 1 0) surface exceeds 2 monolayer (ML) needles are formed. The actual shape, size and number of the needles depends on the substrate temperature, the flux of molecules during growth
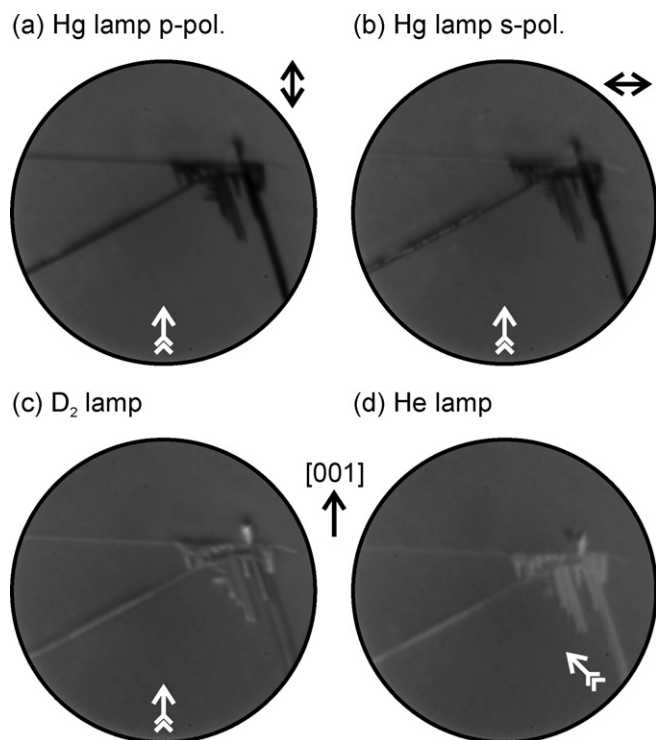


(a) Hg lamp p-pol.  (b) Hg lamp s-pol.

(c) D₂ lamp  (d) He lamp

[001]

**Fig. 1.** PEEM images recorded from a Ag(1 1 0) surface after deposition of about 6 ML of α-6T at 334 K. For the photoelectron excitation different light sources were used: (a) Hg lamp with p-polarized light (4.9 eV), (b) Hg lamp with s-polarized light, (c) D₂ lamp (6.4 eV) and (d) He lamp (21.2 eV). The field of view is approximately 35 μm. Each image is a sum of 50 individual snapshots. The gray value for the wetting layer in (a), (c) and (d) was set to the same value to account for the different lamp intensities. The brightness of image (b) is increased compared to (a) by a factor of 4.75 indicating a strong polarization dependance of the photoemission yield. The propagation directions of the incident light are indicated by the white arrows.
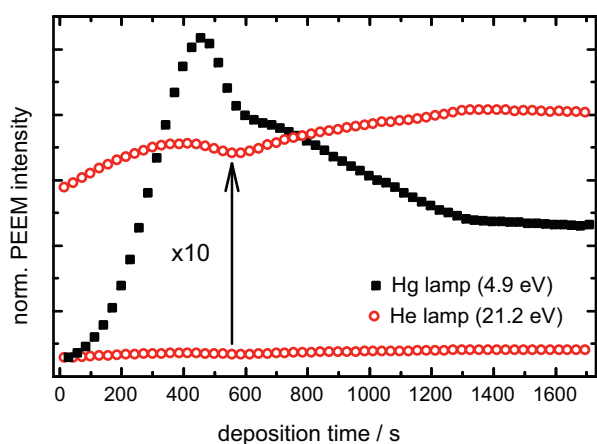


**Fig. 2.** Transients of the PEEM intensity recorded during the deposition of α-6T on the Ag(1 1 0) surface at 377 K. During deposition the illumination was switched periodically between Hg and the He lamp. The data points shown represent an area on the surface which is not overgrown by an α-6T crystallite. For comparison, the transients were normalized to the same initial intensity.

as well as the number and the kind of defects on the surface. By monitoring the growth of such structures in the PEEM – see Figs. 2 and 3 – one finds that such structures consist of several elongated crystallites which have a common nucleation center. The nucleation most often starts at impurities or defects on the surface so that one can assume that the mobility of the molecules even at room temperature is quite high.

For the excitation of the photoelectrons different light sources have been used. Depending on the photon energy, on the uniform background a number of needles appear dark (Hg lamp) or bright (D₂ and He lamp). In the case of the Hg lamp ($h\nu$ = 4.9 eV), the energy of the photons is not sufficient to overcome the ionization potential of the molecules bound in the crystallites, but only the one of the silver substrate for which a work function of 4.25 eV is reasonable [10]. As reported by Grobosch and Knupfer, the ionization potential of a thick film of α-6T on polycrystalline silver is 5.3 eV which is higher than the energy of the supplied photons [11]. Even in the case that the photoelectrons are generated in the silver substrate they will have to pass through the organic layer. As the mean free path of the photoelectron excited by the Hg lamp can be estimated to be as short as 1.5 nm the electron emission is strongly attenuated already by a couple of layers [11,12]. The mean coverage with α-6T for the sample shown in Fig. 1 is 6 ML of flat lying molecules. Even assuming a wetting layer consisting of two layers of flat lying molecules – see below – the height of the crystallites will be several times higher than the mean free path of the electrons. Therefore, the crystallites appear dark if the Hg lamp is used for the photoelectron excitation.

If the maximum photon energy is increased by using a D₂ or He lamp, the photons can stimulate the emission of electrons from the molecules into the vacuum. In this case, it is expected that the α-6T crystallites appear no longer totally dark as with the Hg lamp. Indeed, the D₂ and the He lamp are both suitable to excite photoelectrons from the organic material but the actual contrast in both cases (see Fig. 1) is quite different for several reasons: (i) the direction of the incident light is not the same and (ii) the absorption of the light and the photoemission process in the organic dye strongly depend on the spectral distribution. For the D₂ lamp the facets of the needles facing the lamp are brighter than the ones on the opposite side. This 'shadowing effect' suggests that the absorption length for the deep UV light should be smaller than the width of the needles. For the helium lamp this shadow effect is almost absent indicating that the HeI emission line is only weakly absorbed by the organic material.

In order to investigate the growth kinetics, we have monitored the local PEEM intensity during the thin film growth as depicted in Figs. 2 and 3. We first want to discuss the excitation by the Hg lamp as shown in Fig. 2. Just after opening the shutter of the evaporator, we observed a steady and spatially uniform increase of the photoemission yield. A maximum of the intensity is reached after 450 s. Then the intensity drops until it reaches a steady state at about 1300 s. This time also marks the first visible nucleation of 3D crystallites. In fact, the maximum of the PEEM intensity transient coincides with closing of the first layer of α-6T on Ag(1 1 0). The monolayer effectively lowers the emission barrier for electrons excited from the substrate due to the formation of an interface dipole. Grobosch et al. report a lowering of the work function by ~0.7 eV [11]. Our earlier STM/PEEM study [13] suggests that for submonolayer coverage the molecules form rather disordered structures in which the molecules are highly mobile. Indeed, we observed also small domains (expanding in one direction up to 100 nm) in the STM experiments which exhibit a well ordered superstructure. Since this islands are homogenously distributed across the surface and too small to be resolved individually in the PEEM, the electron yield just shows a uniform increase during the growth of the first layer.