Surface plasmon microscopy for monitoring laser deposition of nanographene monolayer

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Surface Plasmon Resonance (SPR) spectroscopy und microscopy (SPM) allowed for the first time to analyze the deposition of laser-desorbed nanographene. Via SPR we proved an alteration of the optical layer thickness, which can be attributed to the mono- multilayer transition. With SPM we study the homogeneity of Pulsed-Laser Deposition (PLD) over a cross-section of 3mm.

1 Introduction

Nanographenes are promising candidates for organic electronics. They allow for the development of easily produced, cost-effective, large scale electronics. Haxabenzocoronene (HBC) belongs to the family of nano (molecular) graphenes [1]. Layers of solubilized HBC-C_{12} could already be employed [1] as solar cells or light-emitting diodes (fig. 1 left, face-on) and as field-effect transistors (fig. 1 right, edge-on). Indeed, the solubility of HBC is substantially increased through the use of C_{12}-chains, although at the expense of a reduced concentration of the electroactive HBC unit. Thin layer fabrication of HBC without C_{12} chains requires gas phase processing either by sublimation at 700°K and 10^{-9} mbar [2], which is technically very demanding or pulsed laser deposition (PLD) [3]. Here we employ PLD as an alternative method and investigate the growth kinetics and the surface distribution of HBC molecules by SPR and SPM

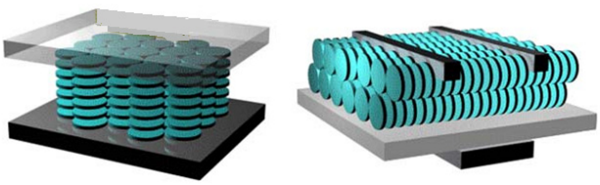

***Fig. 1** left: face-on orientation of HBC and right: edge-on orientation of HBC* [1].

2 SPR and Surface Plasmon Resonance Microscopy (SPM)

SPR scans can monitor optical thickness variations δL

$$\delta L = \delta n \cdot d + n \delta d \tag{1}$$

where n denotes the refractive index of the film and d the film thickness respectively.

In SPM surface plasmons illuminate the thin film sample under investigation. In this way sample areas under SPR will lead to low reflectivity values, i.e. dark image areas contrasting samples areas away from SPR. Assuming a homogeneous refractive sample index. The image contrast in SPM is determined by the difference between the reflectivity of different sample areas. The lateral image resolution is determined by the propagation length L_z of the surface plasmon

$$L_z = \frac{\varepsilon_m'^{\,2}}{\varepsilon_m''} \left(\frac{\varepsilon_d \cdot \varepsilon_m'}{\varepsilon_d + \varepsilon_m'} \right)^{-3/2} \cdot \frac{\lambda}{2\pi} \tag{2}$$

With $\varepsilon_m' = -12$ and $\varepsilon_m'' = 1.33$ for gold, $\varepsilon_d = 1$ for air and $\lambda = 633\,nm$ equation 2 yields to

$L_z \approx 9.5\,\mu m$.

3 Pulsed Laser Deposition

The PLD setup is depicted in fig. 2. For the HBC sublimation a pulsed nitrogen laser (λ = 337 nm, τ = 3 ns, repetition rate 60 Hz) has been employed. For a fragmentation-free sublimation of the molecules the laser power is adjusted to 53 µJ. Through a screw-like movement of a rotating rod covered by HBC molecules a constant desorption has been guaranteed [3]. During deposition process the pressure a pressure of p~10^{-6} mbar is maintained. In this way a HBC nanographene film has been deposited onto the gold substrate.

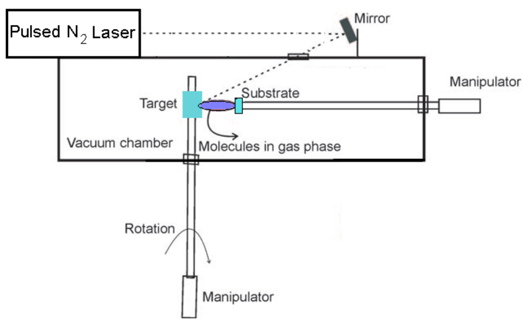

***Fig. 2** PLD setup for deposition of nanographene [1].*

4 Mono-multilayer transition in SPR kinetics

For monitoring the HBC-film growth kinetics by SPR spectroscopy at 633 nm a flame annealed template stripped gold (111) sensor has been prepared. The kinetics is shown in fig. 3 (red curve, left axis). At a SPR shift of $\delta\theta \approx 0.13$ ° the red curve shows a kink, which according to equation 1 corresponds to a change in the optical thickness rate dδL/dt. The SPR kinetics divides the process into two parts: 1st $\delta\theta < 0.13$ ° and 2nd $\delta\theta > 0.13$ °.

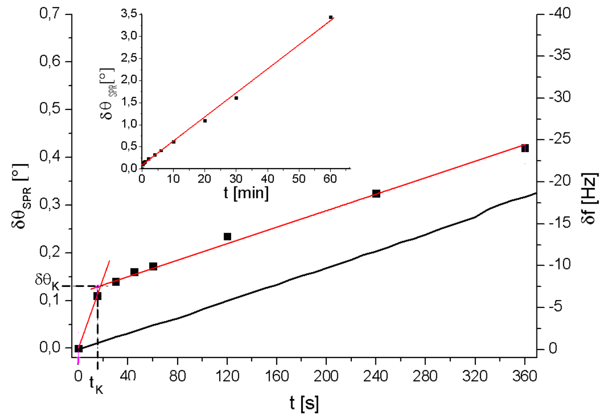

Fig. 3 *SPR (left axis) and QCM (right axis) kinetics, i.e. SPR-shift $\delta\theta_{SPR}$ and resonance frequency shift δf respectively, both versus pulsed laser deposition time. t_K and $\delta\theta_K$ mark an abrupt change of dθL/dt (K-Kink)*

QCM has been used for monitoring the mass deposition rate of the deposition process. A crystal oscillator (6 MHz, gold surface) has been inserted as target into the vacuum chamber (SQM-160, Sigma Instr.). The black curve (right axis) shows the change of resonance frequency Δf of the crystal oscillator. The constant linear mass deposition is clearly obvious.

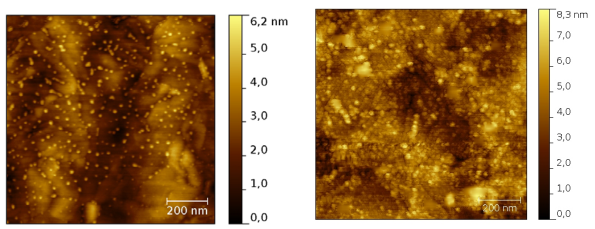

Fig. 4 *left: AFM image with sub monolayer HBC ($\delta\theta <$ 0.1 °). Right: AFM image of sample surface with complete coverage ($\delta\theta_{SPR} \approx 0.13$ °)*

In fig. 4 AFM pictures show that for a shift $\delta\theta_{SPR} <$ 0.1 ° only single clusters are present and at $\delta\theta_{SPR} \approx 0.13$ ° a complete coverage manifests itself.

For a thick HBC-film ($\delta\theta \approx 3.5$ °) a thickness of 10.5 nm has been measured using a profilometer and with a fitting procedure based on a transfer matrix algorithm a refractive index of n = 2.06 and an absorption coefficient of $\kappa = 0.06$ have been determined.

5 Imaging structured HBC-monolayers by SPM

For SPM-imaging a HBC film of app. 0.5 nm thickness has been deposited through a TEM-grid (Ø = 3.05 mm, mesh size app. 95 µm) onto the gold substrate. The laser beam has been expanded to app. 3 mm, and the sample is imaged in reflection mode through a zoom lens (VZM 200i Edmund Optics) and a CCD camera (Lumenera Infinity 3.1). The dark areas were covered by the grid during the deposition. The lateral resolution is limited by the propagation length of the surface plasmon and amounts here to app. 9.5 µm (see equation 3).

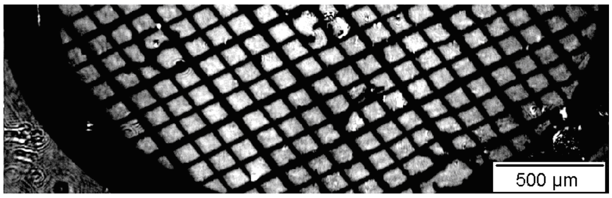

Fig. 5 *SPM image of app. 0.5 nm thick HBC layer*

6 Conclusion

SPR spectroscopy and SPR microscopy are powerful tools to monitor the nanographene deposition process with Ångström resolution in thickness. SPM in particular allows the investigation of deposition homogeneity in refractive index and layer thickness over a lateral range of 3 mm. A significant kink in SPR-kinetics might indicate a mono-to multilayer transition in deposition. With AFM the initial part has been identified as the phase of sub monolayer formation.

Literature

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