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Spectrum Instruments

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Polymers & Thin organic Films

Application Notes

SPM METHODS FOR POLYMER INVESTIGATIONS

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The polymers investigations by SPM have a number of advantages.

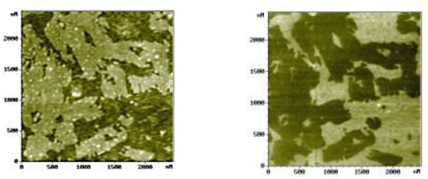
High resolution, which allows visualizing the objects of several nanometers size.

Minimal requirements to sample preparation.

Wide range of different methods to investigate the polymer's properties.

All of the results described below are obtained on commercial SPM SOLVER P47.

When we use the contact mode the tip-sample interaction is strong and soft materials like polymers can be either deformed or damaged. Usually good quality topography measurements of the polymers with contact mode are difficult in air. The using of soft cantilevers and measurements in liquids reduce the tip-sample interaction, but contact with liquid can change the sample structure. Despite these disadvantages in some cases contact regime can be used for nanotribology experiments and also for revealing the different components in composites [1,2]. This is achieved by measurements of the lateral deflection of the cantilever (lateral force microscopy (LFM)) that depends on the friction force. The rough surfaces make difficulties for the interpretation of the results, because lateral deflection of the cantilever depends not only on friction but also on topography. Fig.1 shows topography (a) and LFM image (b) of Langmuir-Blodgett film of blend of two components (p-octadecylcarboxyazobenzene-p'-sulphonamide and copolymer octafluoroamilacrylate and metacrylicacid). Despite visible damages on the topography the areas with different friction are clearly seen on LFM image. The bright areas (the higher friction force) correspond to polymer.



a b

Fig.1. Topography (a) and lateral force (friction) distribution (b) for two-component LB-film.

The using of semicontact mode allows eliminating the destructive action of the lateral forces, which exist in contact mode. The tip-sample interaction in semicontact mode is greatly reduced in comparison with contact mode. This is especially important for easily injured polymer surfaces. Fig.2a shows the topography of the same LB film acquired in semicontact mode. Increasing of the quality of the image is clearly seen from comparison Fig1a and Fig.2a.

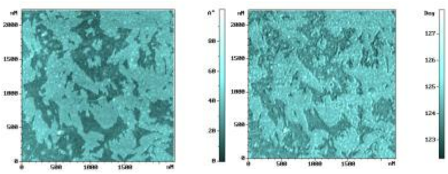


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Fig.2. Topography (a) and phase image (b) for two-component LB-film.

It is convenient to introduce coefficient k=mag/mag0, where mag0 is amplitude of free oscillations of cantilever, mag is amplitude of the cantilever oscillations during scanning (set-point). The minimum possible mag0 and maximum possible mag are desirable in semicontact mode for topography (height) imaging. Force acting on the sample is minimal when k close to 1. As a result the quality of the topography image will be better. For example the topography of Langmuir-Blodgett film of cyclolinear polyorganosiloxane is shown on Fig.3. Collapsed film was deposited on mica by Langmuir method. The islands of the second and third layers lay on the monolayer. The height of the every layer is about 1nm. The cantilever amplitude of free oscillations is 7nm for Fig.3a and 60nm for Fig.3b. In both cases k=0.97. It is clear seen that not only quality of the image reduce after increasing of the amplitude but also the destruction of the film is observed (lower part of the Fig.3b).

In some cases the amplitude-image (feedback error) helps to distinguish the small features on the topography. The amplitude-image is signal of error,

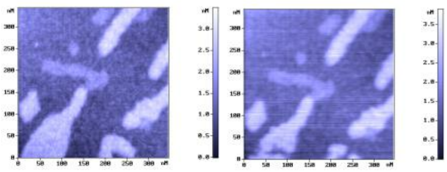

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Fig.3. Topography of the LB film obtained with different cantilever amplitude: a) 7nm, b) 60nm.

which exists due to non-ideal feed back loop. Only small irregularities are visible in this case because smooth topography is tracked by feedback. The Fig.4 presents the spherulite organization of polypropylene. The height-image (Fig.4a) and the amplitude-image (Fig.4b) were obtained simultaneously. It is seen that lamellae structure of spherulites is more visible on Fig.4b. The contrast ofthe amplitude-image will increase after either the scanning velocity increasing or feedback gain decreasing. The optimal scanning parameters for amplitude-image should be particularly selected for every sample.

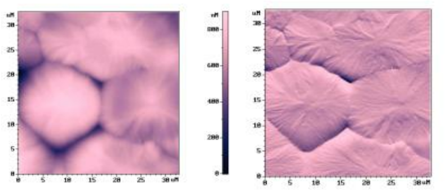

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Fig.4. Topography (a) and feedback error image (b) of the polypropylene spherulites.

Strong contrast is the typical feature of the imaging of the oscillating cantilever phase shift. The phase image is acquired by simultaneous measuring of topography and cantilever phase shift during scanning in semicontact mode. This strong contrast can be explained by the dependence of the phase shift on the surface properties. The phase shift depends not only on topography but also on adhesion, elasticity, and damping. Because of it phase image enable to use it for revealing the surface areas with different properties. For example it is possible to reveal the distribution of the components in composite material, the distribution of the amorphous and crystalline phases. Fig.2b demonstrate the phase-image for two-component LB film that obtained simultaneously with Fig.2a. The dark areas on Fig.2b correspond to areas with greater phase shift. This phase contrast is explained by both different hardness and adhesion of the different components. Fig.5 shows the topography (Fig.5a) and value of mag*sin(phase) (Fig.5b) obtained simultaneously for poly(diethylsiloxane). The sample is thin film of polymer deposited on silicon surface by rubbing. The direction of rubbing is from left lower corner to right upper corner. Dark background on Fig.3b is the amorphous polymer. The lamellae placed perpendicular to the rubbing direction are embedded into the amorphous polymer and consist of folded molecular chains. The lamellae are mesomorphic (partially-ordered) state of PDES. The molecules in lamellae are stretched along rubbing direction. The strips in lamellae stretched along rubbing direction, which are clearly seen on Fig.3b, can be compared with molecular structure of the lamellar blocks.

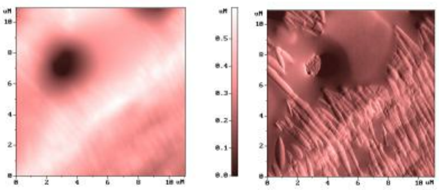

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Fig.5. Topography (a) and amplitude*sin(phase) image (b) for the poly(diethylsiloxane).v

Fig.6 demonstrates the crystalline structure of the polyethyleneoxide sample that was obtained by cooling of the melt. The lamellae are tilted at different angles with respect to surface. The grains of various sizes are visible on the edges and on the sides of the lamellae.

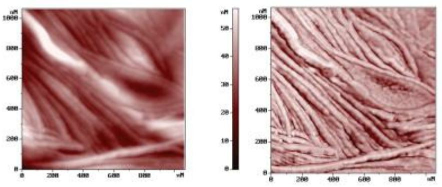

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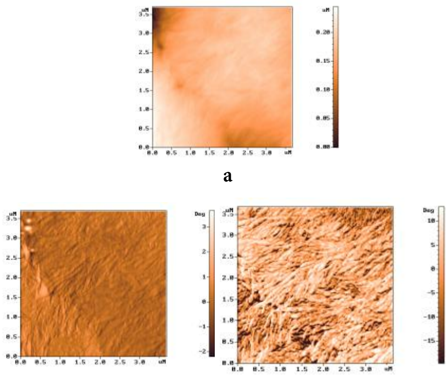
Fig.6. Topography (a) and phase image (b) of polyethyleneoxide.

The phase image strongly depends on set-point, i.e. on strength of the tip-sample interaction. The influence of the material properties on phase-image usually increases with decreasing k (by decreasing mag) [3,4]. The numerical simulation in [3] demonstrated that in general the influence of the sample properties on the cantilever response is intricate when k is small. But in the some cases it is possible to connect the phase changes with the changes of the some of surface properties. Fig.7 shows the boundary of the two spherulites of poly(buthyleneterephtalate)-poly(tetramethyleneoxide) (PBT-PTMO) block-copolymer. Crystalline phase of copolymer consist only PBT, amorphous phase is combination of amorphous PTMO and uncrystallized PBT. The topography and phase image obtained simultaneously are shown on Fig.7a and Fig.7b, k=0.95. The phase image for the same area for k=0.7 imaged on Fig.7c. The increasing of contrast on Fig.7c is explained by influence of the local stiffness. The dark areas on Fig.7c can be associated with softer amorphous phase.



a

b c

Fig.7. Topography (a) and phase images (b, c) obtained with different set-point.

The force modulation imaging is also used to study the local stiffness. In this case the modulation of the probe-sample spacing during contact mode by scanner oscillations leads to cantilever oscillations. The different response of the cantilever from areas with different stiffness can be observed. Fig.8a and Fig.8b show topography and force-modulation image (cantilever amplitude) obtained simultaneously for the sample of two-component LB film. The light areas on Fig.8b correspond to higher cantilever amplitude, i.e. higher hardness. These areas are polymer. The substrate can influence on the results of the LFM, force-modulation mode etc. when thin film are studied [1,2].

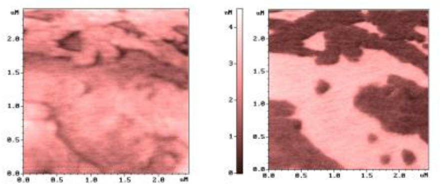


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Fig.8. Topography (a) and force-modulation image (b) for two-component LB-film.

Adhesion force microscopy (AdFM) allows mapping the differences in adhesion. The dependence of the cantilever deflection on the piezotube location is obtained in each point of the scan. The distribution of the minimum of this dependence for full scan gives information about differences in adhesion. Fig.9 shows the topography (a) and the AdFM image (b) for the sample of two-component LB film. The dark areas (polymer) on Fig.9b correspond to higher adhesion. This different adhesions as well as contrast of the force-modulation image explain the phase contrast on the Fig.2b.

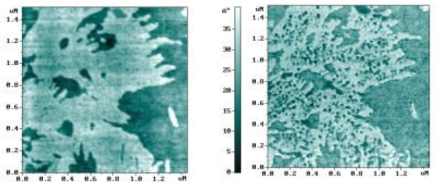

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Fig.9. Topography (a) and adhesion force distribution (b) for two-component LB-film.

The sample of two-component LB film consists of polar materials. NT-MDT SPMs are useful tools to studying the electric properties of this sample.

The using of the SMENA for high temperature measurements (up to 300°) allows investigating various processes such as crystallization, melting etc. The growth of the polypropylene spherulite in the melt observing with this type of SPM demonstrates this possibility

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