



Dynamic scaling and kinetic roughening of poly(ethylene) islands grown by vapor phase deposition



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ABSTRACT

Vapor phase deposition of poly(ethylene) is shown to produce uncross-linked thin films consisting of linear $(\text{CH}_2)_{100}$ oligomers with narrow molar mass distribution of dispersity $D_M = 1.10$. Early stages of the film formation are characterized by the growth of two-dimensional compact islands of constant 7–8 nm thickness. The transversal evolution of islands is studied in the context of the Dynamic Scaling Theory. The aggregation regime is found to be valid in a narrow range of coverage $0.1 < \theta < 0.3$. The critical island size is estimated to be $i = 1$. Kinetic roughening of the growing front gives a set of the scaling exponents $\alpha_{loc} = 0.67$, $\alpha_s = 0.85$, $\beta = 0.33$ ($\beta = 0.2$ for the late stages of growth) and $z = 2.2$ that does not fit into any of the known universality classes. Macromolecular relaxation at the island edges is suggested to explain the observed inconsistency.

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1. Introduction

Dynamic phenomena occurring at initial stages of gas phase deposition of organic thin films have been attracting keen scientific attention. This was driven mainly by the progress achieved in organic molecular beam deposition (epitaxy) (OMBD/OMBE). OMBD enjoys the benefits of solid but easy-to-vaporize organic materials that are transported through vacuum and condensed on solid supports in the form of thin films. Since OMBD stems from semiconductor Molecular Beam Epitaxy (MBE), it inherited the research focus on optoelectronic properties of deposits and most of the studies were done on macrocyclic planar or polycyclic aromatic compounds such as phthalocyanines, perylenes and others [1]. The main difference that organic deposition brings in comparison to inorganic growth is related to anisotropy of properties inherent for organic molecules and, as a consequence, to polymorphism of resultant organic structures. In contrast to atomistic inorganic deposition, organic molecular conformation and orientation on surfaces are additional parameters that tremendously diversify the kinetics of growth.

Understanding the processes occurring at deposition of thin polymeric films may be even more challenging. Many organic molecules studied so far, albeit diverse in nature, exhibit a rigid polycyclic core. Their configuration on surfaces can be analyzed with the knowledge

of particular molecular dimensions. For example, flat-lying or upright-standing orientation can be deduced simply by measuring the submonolayer thickness by Atomic Force Microscopy (AFM) [2–12]. Larger organic molecules (macromolecules, polymers) have more intramolecular degrees of freedom and can be expected to exhibit even richer and more complex behavior on surfaces. For the simplest case of poly(ethylene) (PE), single bonds $-\text{CH}_2-$ possess significant extent of rotational freedom even though steric hindrances restrict free rotations [13]. Configurational versatility of the chain can be further affected in the proximity of solid interfaces and this may also influence the way how macromolecules diffuse over surfaces. Unfortunately, dynamics of macromolecules at solid/vacuum interface has been rarely studied. In many cases this is given by the lack of diagnostics tools and by experimental difficulties [14]. The most obvious one is that vaporization of polymers is in many cases difficult as polymers tend to degrade when heated to elevated temperature. For this reason, polymeric films have been generally deposited from solutions and melts. Nevertheless, it has been shown that certain polymers including PE can be processed by thermal vapor phase deposition to fabricate thin films. The first reports [15–20] were focused on applicability of the method as such and on basic characterization of resultant films. Later, formation of small rod-like crystals during initial stages of PE deposition [21,22] as well as of bigger islands [23,24] was detected; however, kinetics of growth was hardly addressed.

This work aims at studying dynamic phenomena occurring during vapor phase deposition of PE and elucidation of the mechanisms of

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the film growth. In OMBD processes, formation and evolution of islands was often analyzed within the frames of a Dynamic Scaling Theory (DST) [25,26], a universal concept of diffusion-mediated growth that interrelates island density, average island size and coverage. Furthermore, kinetic roughening of thin films was often explored by calculating the critical exponents and by assigning them to known universality classes of surface growth. The particular aim of this work is to check the applicability of the DST to deposition of the PE islands, to correlate such growth with that of other OMBD as well as with theoretically predicted universality classes and thus to highlight most probable mechanisms of the surface evolution.

2. Experimental

The experiments were performed in a vacuum chamber pumped with rotary and diffusion pumps to the base pressure of 10^{-3} Pa. The depositions were run in argon under 1 Pa working pressure and 5 sccm flow rate. PE (Sigma-Aldrich) was loaded into an electrically heated crucible which was brought to a temperature of about 300 °C at which depolymerization of PE was performed. Polished silicon substrates were ultrasonically cleaned in acetone, ethanol and distilled water prior to deposition. Silicon with a native SiO_2 layer was used as the most common flat, inert substrate for organic depositions. The substrates were introduced into the chamber normal to and 10 cm above the crucible via a load-lock after adjusting the deposition rate. The deposition rate was monitored by Quartz Crystal Microbalance (QCM) placed in-plane with the substrates. The frequency shift of QCM was re-calculated to the deposition rate by measuring ellipsometrically (Woollam M-2000DI) the thickness of the 30–40 nm films and by relating it to the deposition time. For most of the experiments, the deposition rate was maintained at 11 nm/min which corresponded to the QCM frequency shift of 20 Hz/min. A number of depositions were performed with different deposition rate; this will be discussed further where relevant. The temperature of the substrates was checked by a thermocouple not to exceed 30 °C even at longest depositions.

The films were analyzed ex-situ by an Atomic Force Microscope (Ntegra Prima, NT-MDT) in a semi-contact mode under ambient air conditions. Soft silicon cantilevers (NSG03, NT-MDT, typical spring constant $k = 1.7$ N/m, typical radius of curvature $r = 10$ nm) were used at highest setpoint possible to avoid exerting excessive force on the polymeric samples. The AFM images were acquired with 256x256 datapoint resolution at 0.5 Hz scan frequency. The AFM images were flattened by Image Analysis software (NT-MDT, built 3.5.0.) to remove the overall slope of the surface. No other processing was applied.

The chemical composition of the 15–20 nm thick films was analyzed by X-ray Photoelectron Spectroscopy (XPS, Phoibos 100, Specs, wide spectra acquired at pass energy of 40 eV and normal take-off angle) and by Fourier Transform Infrared Reflection Absorption Spectroscopy (FTIR-RAS, Bruker Equinox 55, 250 scans for each sample at 2 cm^{-1} resolution, the films were deposited on gold covered silicon).

Gel permeation chromatography (PL-GPC 220 with PL-220DRI refractive index detector, columns 3x PL gel $10\ \mu\text{m}$ MIXED-B, 300×7.5 mm, with guard column PL gel $10\ \mu\text{m}$ MIXED-B, 50×7.5 mm) was used to establish the molar mass distribution of the deposited films as well as of the precursor PE. The sample solutions were prepared in filtered 1,2,4-trichlorobenzene for chromatography (Scharlau) containing 0,025 wt% of an antioxidant Santonox R to prevent oxidative degradation of polymers. The GPC analysis was performed at 160 °C. For calibration, poly(styrene) standards were used (Waters a Polymer Laboratories).

Nuclear magnetic resonance (NMR) solid-state ^{13}C CP/MAS spectra were measured on a Bruker Avance 500 WB/US NMR spectrometer operating at 125.78 MHz. The MAS frequency was 10 kHz, recycle delay 6 s; 10 000 spectra were accumulated. The contact time was set to 1 ms. The spectra were externally referenced to the signal of the carbonyl carbon of glycine.

3. Results and discussion

3.1. Chemical composition

In OMBD, dimensions and chemistry of the species to be deposited are known *a priori* since it utilizes organic compounds of well-defined chemical structure. In the case of polymers being used as precursors for Physical Vapor Deposition (PVD), this issue should be addressed more thoroughly. Nature and size of depositing species may have significant influence on the kinetics of the surface diffusion and they are therefore of great importance. However, the products of polymer thermal degradation may not be necessarily the replica of the original macromolecules, let alone the fact that molar mass distribution of thus evaporated films is usually shifted to lower values [27].

In this work, chemical composition of the films prepared as a result of PVD of PE was studied by XPS, FTIR and NMR. XPS was used only to prove that the elemental composition of the films is 100% carbon (without accounting for hydrogen undetectable by XPS). No other elements were detected. High-resolution C 1s spectra (not shown) are symmetric and typical for PE.

The FTIR spectrum given in Fig. 1 shows that the films are chemically close to polyolefins. Well-resolved absorption bands of asymmetric and symmetric stretching vibrations of the CH_2 groups are located at 2918 and 2851 cm^{-1} , respectively. Deformation vibrations of these groups are located at 1463, 1377 and 910 cm^{-1} in close agreement with the infrared spectra of other polyolefins [28]. The presence of the small band at 1641 cm^{-1} indicates the minor contribution from the $\text{C}=\text{C}$ bonds that are known to be formed as a result of radical disproportionation reactions during thermal degradation of PE [29].

The NMR analysis complements the findings of FTIR spectroscopy. Fig. 2 shows the solid state ^{13}C CP/MAS NMR spectrum of the PE film where the most intensive peak at 32.4 ppm and the sub-peak at 30.1 ppm belong to the methylene units in the crystalline and amorphous phase, respectively [30]. (Note that the NMR measurements were performed on the thicker films scratched off from the substrates and hence the crystalline/amorphous phase ratio may not exactly correspond to the ultra-thin coatings). The peak at 14.6 ppm is attributed to the methyl moieties which are the end groups of the PE chains. Comparison of integrated intensities of the peaks gives the value of 4 CH_3 groups per 100 CH_2 groups. The entire up-field region at 0–40 ppm is characteristic for linear PE without pendant aliphatic groups. The down-field region at 100–150 ppm is characterized by the presence of the subtle, yet discernible peaks (for details see the inset in Fig. 2). These belong to the unsaturated carbon in different $\text{C}=\text{C}$ configurations. Low intensity of these peaks allows estimation of their concentration to be less than one molar percent of the CH_2 groups.

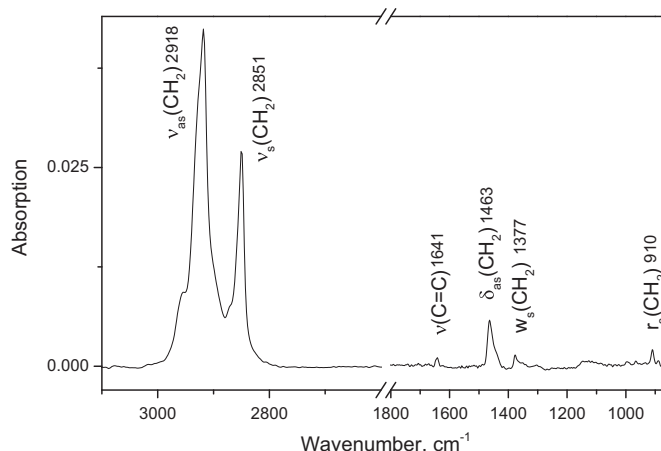


Fig. 1. The FTIR spectrum of the film prepared by vapor phase deposition of PE on Si.

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