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Self-assembly of dodecaphenyl POSS thin films

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ABSTRACT

The self-assembly abilities of Dodecaphenyl Polyhedral Oligomeric Silsesquioxane thin films on Si(1 0 0) surfaces were studied. Due to their thermal properties – relatively low sublimation temperature and preservation of molecular structure – cage type silsesquioxanes are ideal material for the preparation of a thin films by Physical Vapor Deposition. The Ultra-High Vacuum environment and the deposition precision of the PVD method enable the study of early stages of thin film growth and its molecular organization. X-ray Reflectivity and Atomic Force Microscopy measurements allow to pursuit size-effects in the structure of thin films with thickness ranges from less than a single molecular layer up to several tens of layers. Thermal treatment of the thin films triggered phase change: from a poorly ordered polycrystalline film into a well-ordered multilayer structure. Self-assembly of the layers is the effect of the π–stacking of phenyl rings, which force molecules to arrange in a superlattice, forming stacks of alternating organic-inorganic layers.

1. Introduction

Silsesquioxanes are hybrid, organic-inorganic compounds consisting of a silica core, usually in the form of a ladder, cages or open cages with organic groups attached to each silicon. The first syntheses and identification of isolated silsesquioxane molecules by Scott [1] occurred over 60 years ago. Since then, the wide range of possible molecular configurations of polyhedral oligomeric silsesquioxane (POSS) molecules has proved to be an attractive subject of study. POSS molecules combine the outstanding hybrid architecture, in which an inorganic framework provides stability and endurance, and the organic substituents (active or inert) gives a wide range of functionalities [2,3]. Moreover, POSS can bind chemically or blend physically with accompanying materials: polymers [4] or biological systems [5]. Moreover, POSS molecules covalently bonded with polymer chains [6,7] or with mesogens [8] can be used in a “bottom-up” approach to create self-assembled structures. In addition, the electronic structure for conjugated molecules, as in the studied system, could be strongly alter by interaction on the film/substrate interface [9,10]. This can lead to the formation of a completely different structure in the case of ultra-thin films comparing to the bulk material.

The aim of these presented studies is to show direct evidence of the self-assembly of POSS molecules with phenyl substituents. The observed self-assembly process was induced by non-covalent intermolecular interaction on the surface. Typically, 2D self-organization processes [11] or 3D [12] ones on the surface are observed for flat-architecture molecules. The symmetry of the molecule plays a key role in the kinetics of thin film growth as it was recently studied by the Lorch et al. [13]. In these research, POSS molecules deposited on Si(1 0 0) surfaces by the molecular beam technique underwent a similar self-assembly process, although its structure is almost spherically symmetrical. The key role in the process is played by the π-stacking interactions that lead to the formation of a new structure resembling the smectic phase.

2. Experimental

2.1. Thin film preparation

Thin film preparation as well as substrate treatment and cleaning were performed in Ultra High Vacuum conditions. The custom designed UHV system built by PREVAC sp. z o.o. consisted of two chambers. The main chamber was dedicated to clean processing such as sample annealing (up to 1400 °C), Ar^+ ion sputtering, RF plasma treatment and e-beam evaporation. The chamber pumped by a turbomolecular pump along with an ion one enabled a base pressure in the lower range of 10^{-8} Pa to be achieved. The second preparation chamber equipped with an effusion cell dedicated to low sublimation temperature materials (Dr. Eberl MBE-Komponenten, GmbH) with a base pressure in the lower range of 10^{-7} Pa was used for POSS deposition.

Dodecaphenyl POSS – $Ph_{12}T_{12}$ ($(C_6H_5)_{12}O_{18}Si_{12}$) powder from Hybrid Plastics Inc. was used as a source material for evaporation in the effusion cell. Each time before thin film deposition, the material was degassed for several hours at a temperature just below the sublimation temperature. The base pressure in the preparation chamber during

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sublimation was less than 5×10^{-6} Pa. The deposition rate was checked each time both before and after deposition with a quartz crystal microbalance. The typical deposition rate was 3.0 Å/min at 215 °C. As a substrate, Si single crystals with a polished and well oriented (1 0 0) surface ware used. *In-situ* cleaning procedures consisted of degassing at 350 °C for 24 h and a few cycles of RF Ar^+ plasma cleaning with subsequent annealing, also at 350 °C. The cleaning procedure proposed by Kim et al. [14] was sufficient to remove native oxide from the Si(1 0 0) surface, but too an overly annealing temperature was not sufficient for surface recrystallization; thus, all presented results correspond to those thin films grown on amorphous, but atomically flat surfaces. Thin films were deposited at room temperature and then samples were transferred to the main chamber and heated up to 200 °C for 1 h to reorganize the thin film structure.

Since all the measuring techniques used were *ex-situ*, each time a different thickness was investigated, a new sample had to be made *de novo*. The reuse and introduction into UHV of a pre-made sample was not possible because of contamination from the ambient atmosphere.

2.2. Measurement techniques

For thin film thickness and composition analysis, X-Ray Reflectivity (XRR) was applied. By simulation and fitting of XRR spectra, it is possible to establish the composition, roughness and the thickness of layers. XRR measurements were performed using an Empyrean PANalytical diffractometer, equipped with parallel beam optics, a Euler's cradle and with a CuK_α X-ray source. XRR data were fitted using X'Pert Reflectivity 1.3a software by PANalytical [15]. Reciprocal space maps were also collected using the same Empyrean diffractometer, but instead of using a mirror, a high-resolution four-bounce monochromator was used at the incidence beam side Atomic Force Microscopy (AFM) images were collected with a Bruker Nanoscope 8 using PeakForce Tapping mode.

3. Results

From previous studies [16], we have learned that $Ph_{12}T_{12}$ thin film structure differs from that observed for powder specimens. It is not only the question of a lower degree of order. The thin film structure could exhibit a completely new form due to the strong asymmetry of the intermolecular interaction driven by the substrate/film and film/surface. Moreover, we have found that during annealing at a temperature close to the sublimation point, thin film undergoes structural phase change. Grazing incidence x-ray diffraction (GIXD) showed Bragg peaks that could not be associated with those measured for powder specimens. Since the GIXD measurements did not give any clear results (just one or two Bragg peaks being present is not enough to determine the structure), only an indication that the structure of the thin film was probably lamellar, we decided to continue our studies using X-ray Reflectivity (XRR). XRR has proved to be an excellent tool for hybrid – organic/inorganic thin film analysis [17,18], including silsesquioxane thin films [19,20]. The basics of the reflectivity methods as well as kinetic and dynamic scattering theory can be found in many excellent textbooks [21,22], therefore the geometry of the measurement itself will be briefly described. Measurement geometry is defined by the relationship between the wave vector of the incident beam and the scattered beam, and thus the direction of the scattering vector. For XRR measurements, based on elastic scattering, the length of the incident and diffracted wave vector is the same, so the direction of the scattering vector is defined only by the angle between two of them. If during the measurement the relationship is maintained as θ–2θ, the scattering vector will always be perpendicular to the surface of the sample, i.e. to the surface of the layers. In crystallographic terms, the scattering vector "travels" only in the (0 0 l) direction. The results of the XRR measurements are usually plotted as the intensity (normalized to total reflection R) versus length of the scattering vector that is defined as follows: $Q_Z = 4\pi/\lambda \sin\theta$ [$Å^{-1}$]

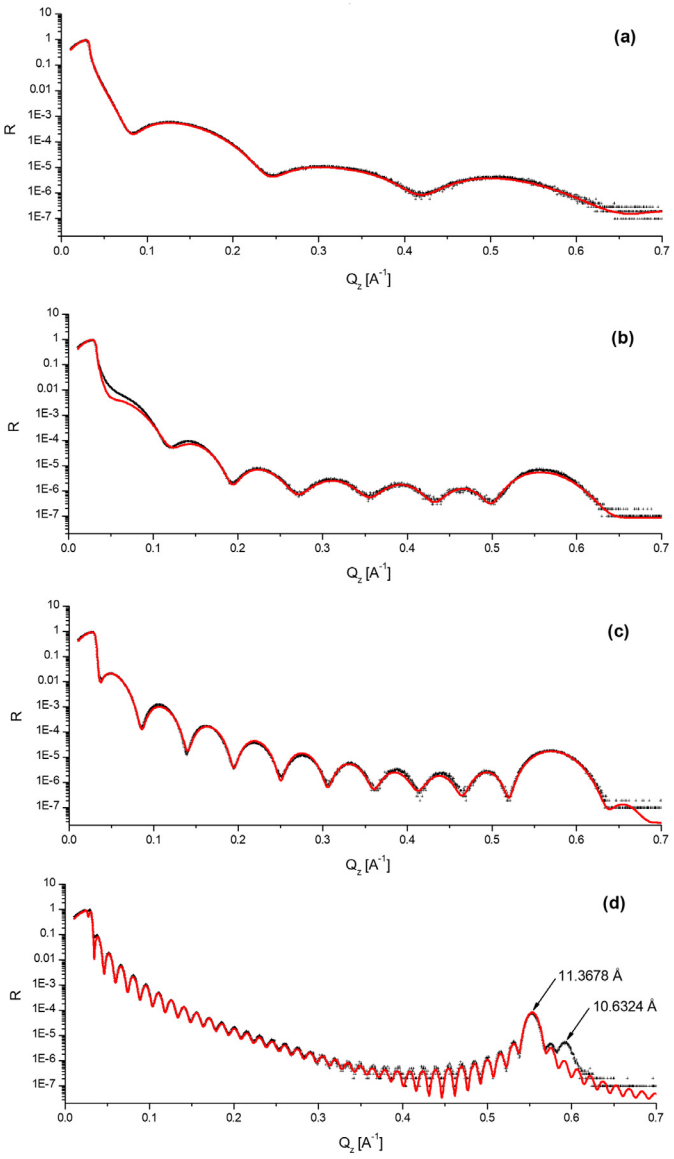

Fig. 1. Specular X-Ray Reflectivity spectra for four different thin film thicknesses: (a) 3.2 nm, (b) 7.7 nm, (c) 10.8 nm, (d) 41.2 nm. Experimental dotted lines are fitted with model solid (red) line. Spectrum (d) includes arrows indicating Bragg reflection and associated distances. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(where λ is the x-ray wavelength and θ is the incidence angle). In the XRR spectra of a well-defined layer on a flat substrate, one may expect characteristic oscillations in intensity (so-called Kiessig fringes). The frequency of the oscillations is proportional to the layer thickness and the oscillation amplitude and its decay is related to the interface and surface roughness.

Fig. 1 shows a series of XRR spectra for four samples; each differs in terms of thin film thickness. Selected from among many, these four represent the most important stages of structure change with thickness. The total thickness of the films was determined by using quartz microbalance measurements and verified by calculations from the fitted model (continuous line). The structural model of the layers will be discussed below. As one can see, all spectra exhibit very distinctive oscillations, which are visible up to 0.7 $Å^{-1}$ (5° θ on the incidence angle scale). The high amplitude of the oscillations indicates a very low roughness and quality of the film-substrate interface and a thin film surface. For the thinnest film (3.2 nm) only three wide fringes are visible, with equal amplitudes, but as the thickness increases (7.7 nm and