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Studies of dodecaphenyl polyhedral oligomeric silsesquioxane thin films on Si(100) wafers ☆

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HIGHLIGHTS

- Dodecaphenyl silsesquioxane ($T_{12}Ph$) thin films deposition by molecular beam technique at UHV condition.
- FTIR measurements on thermal stability of the molecule during the thin film growth as well as after annealing up to 200 °C.
- Ellipsometry measurements for thin film thickness estimation and for optical properties evaluation.
- X-ray Diffraction measurements show two-step ordering process in thin films after several steps of annealing.
- AFM microscopy confirms conducted measurements, demonstrating process of thin film ordering during the annealing.

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ABSTRACT

In this work the spectroscopic and microscopic studies of dodecaphenyl POSS thin films are presented. Thin films have been deposited using molecular beam technique. Due to thermal properties – relatively low sublimation temperature and preservation of molecular structure – cage type silsesquioxanes are perfect to fabricate a thin film by means of physical vapor deposition.

PhT_{12} thin films with thickness varying from 40 nm up to 100 nm, deposited on a Si(100) surface, were studied under high vacuum conditions. The research was focused on the influence of post deposition annealing (from 100 °C up to 200 °C) on molecular structure as well as thin film roughness and optical properties.

A wide range of measuring methods were applied for thin film studies. Fourier Transform Infrared Spectroscopy (FTIR) was used in order to learn molecular structure and stability, Ellipsometry for thin film thickness and uniformity, Grazing Incidence X-ray Diffraction (GIXD) for thin film long range order investigation and finally Atomic Force Microscopy (AFM) for visual confirmation of drawn conclusions.

1. Introduction

The cage silsesquioxanes are under intense studies due to their wide application properties. These compounds are called polyhedral oligomeric silsesquioxanes (POSS) [1] and have the general formula $(RSiO_{3/2})_n$, where $n = 6, 8, 10, 12\ldots$ POSS are known as hybrid organic–inorganic nanocomposites – inorganic core provides stability to the molecule and organic arms can give its specific properties. Cage silsesquioxanes in particular are characterized by chemical and thermal stability, mechanical hardness, low dielectric constant, relatively low sublimation temperature and the preservation of molecular structure [2,3]. Due to these properties POSS are perfect to fabricate thin films by means of Physical Vapor Deposition (PVD). POSS thin films and coatings have a promising application possibilities, such as: photo, electron and X-ray resistant for lithography [4,7], low dielectric constant materials [10], corrosion protection coatings, hydrophobic and self-cleaning coatings [5], and in particular as a support for emitter in OLED (Organic Light-Emitting Diode) fabrication [6]. In this particular application area, obtaining thin film of desired nano-scale thickness and controllable mesoscopic and molecular structure is of a great significance.

Most of reported films of cage silsesquioxanes were coated by sol–gel methods (e.g. spin-coating). However, especially for optoelectronic applications, the well-defined controllable thickness and morphology of deposited films is critical. Thin films made of various POSS molecules tailored with these specific properties

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can be obtained by PVD technique. Polycrystalline films comprised of $(CH_3)_8Si_8O_{12}$ and oriented along one crystallographic direction were obtained on silicon surfaces and quartz plates by Gromilov et al. using Chemical Vapor Deposition (CVD) [4,7]. Nicholson et al. chemisorbed monolayer of $H_8Si_8O_{12}$ onto gold (1 1 1) surfaces [8,9]. There is no information in literature about using PVD method for deposition POSS thin films; however this method was successfully applied by Simonsen et al. to obtain high quality thin films of large organic compound – perylene [11].

2. Experimental

2.1. Thin film preparation

The samples were prepared in a custom high vacuum system (UHV), with the base pressure 5×10^{-9} mbar. As a preparation chamber the six-way cross with DN100CF flanges was used. Each flange was occupied by following devices: magnetic transfer as a sample manipulator equipped with resistive heater and K-type thermocouple, quartz microbalance, vacuum gauge, effusion cell, turbo molecular pump and the fast-entry door.

The home made effusion cell consisted of a small quartz crucible held within a thin Ta filament. A K-type thermocouple was placed in ceramic capillary close to the crucible under the Ta filament. Additionally, two Ta foils were placed around the crucible to thermally isolate the system and ensure that the temperature measured by the thermocouple corresponded to the temperature in the crucible. The dodecaphenyl silsesquioxane – PhT_{12} ($(C_6H_5)_{12}O_{18}Si_{12}$) powder from Hybrid Plastics was used after degassing at a temperature just below the sublimation temperature for several hours. The base pressure in the preparation chamber before and during sublimation was less than 5×10^{-7} mbar. The deposition rate was initially calibrated with a quartz crystal micro balance and was determined to be about 3.0 Å/min, which corresponded to a sublimation temperature of 215 °C. The Si single crystal, with a polished and well oriented (1 0 0) surface was used as a substrate for thin film deposition. *Ex situ* cleaning and degassing at 350 °C in vacuum for several hours was insufficient to remove native oxide from the Si(1 0 0) surface. Thus, all presented results correspond to the thin films grown on amorphous silicon oxide, however with atomic scale flat surface.

2.2. Characterization of the thin films

All presented measurements were carried out *ex situ* at ambient atmosphere and temperature. Fresh samples were prepared each time a new annealing temperature was used for thin film treatment. This was the only way to avoid contamination effects on sample preparation. Therefore, presented results for thin films described as e.g. 50 nm thick, could differ in thickness, but not more than ±2 nm.

The infrared spectrum of PhT_{12} was measured in transmission mode with a resolution of 4 cm^{-1} using Brucker 70 V spectrometer and KBr pellet technique for powder sample.

Thickness and dispersion relations were calculated using experimental data measured with Wollam M 2000 spectroscopic ellipsometer. Optical densities were parallely derived in reflection mode, using Perkin Elmer Lambda 20 spectrometer equipped with an integrating sphere. To estimate sample thickness, the data recorded within wavelength span of negligible optical density (c.a 0.7–3.5 eV, i.e. 1780–350 nm) were fitted with standard Cauchy formula.

Out-of-plain Grazing Incidence X-ray Diffraction patterns were collected using PANalytical Empyrean diffractometer with semi-parallel beam at 0.38° incidence angle.

Atomic Force Microscope images were collected by Nanoscope 8 by Bruker using PeakForce Tapping mode.

3. Results and discussion

3.1. The molecule and thermal stability

Since there are no literature data on thermal stability of dodecaphenyl silsesquioxane in vacuum, the basic question arises: is the molecule stable throughout the whole process of molecular beam deposition? The studies of thermal behavior of PhT_{12} [12] have shown that sublimation of the compound starts at 500 °C and 466 °C, for heating in air or in nitrogen respectively. From that temperature on, the two-step process of weight loss starts, which leads to production of thermally stable residue, which was roughly 50% of initial mass. The two-step process was attributed to the competition between sublimation of the molecule with chemical reactions of the oxidative transformation of PhT_{12} into silica. As expected, the sublimation temperature in vacuum is significantly lower than in ambient pressure. We have found that at around 210 °C the quartz microbalance 15 cm away from the effusion cell starts to show deposition rate of 0.1 Å/min. The most stable deposition rate was reached at 215 °C. We have also found that even if the effusion cell temperature did not exceed 215 °C, after several hours of heating and after few samples made, the deposition rate went to zero. Rising the effusion cell temperature gave no effect and the deposition rate was zero, even though there was still a lot of white powder in the effusion cell crucible. So, the thermal behavior of the molecule in the vacuum is very similar as in comparison to ambient pressure, although in a much lower temperature range.

In order to be completely certain that the thin film consist of PhT_{12} molecule we conducted infrared spectroscopy studies of as-grown and annealed thin films and compared results with initial powder compound. Moreover, experimental spectra were compared with the calculated one. To do so, initial form of PhT_{12} molecule was constructed using silicate anion [12] of mineral milarite. Terminal oxygen atoms of silicate anion were manually replaced by phenyl rings. All phenyls were manually oriented parallel to each other. The model was treated by energy minimization and geometry optimization procedure in the Gaussian 09 program using B98/6-31G(d) method. Optimized shape of the model, frequencies of normal modes along with the displacement vectors and infrared intensities of the normal modes were the results of DFT calculations. Calculated frequencies were scaled using factor of 0.9608. Infrared spectra were constructed assuming a 30 cm^{-1} half-width of calculated bands. DFT calculations were used to assign the corresponding vibration modes of the observed bands in the spectrum. Also, a large convergence between the spectrum obtained on the basis of the calculations and the experimental spectrum confirms the validity of the molecule model being used, while confirming the purity of the compound used. The experimental and theoretical results are presented on Fig. 1. As one can see, all the spectral features are reproduced from the top to the bottom of the figure. Even though, the theoretical model (a) assumes free molecule, the infrared bands for powder sample, and (b) can be easily and unambiguously assigned to the bonds of the PhT_{12} molecule. The most intense peak around 1100 cm^{-1} corresponds to the asymmetrical stretching modes for inorganic core of the molecule. Symmetrical stretching modes for Si—O framework can be attributed to the peak 586 cm^{-1} and 633 cm^{-1}. There is also a very intense signal from the aromatic ring around 490 cm^{-1} (wagging modes) and group of peaks between 697 cm^{-1} and 775 cm^{-1} which corresponds to deformational bending of the phenyl ring present as well. Some stretching modes for C=C bonds overlapped