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Spectroscopic and atomic force microscopy investigations of hybrid materials composed of fullerenes and 3-aminopropyltrimethoxysilane

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ABSTRACT

Fullerene based materials may open a new horizon in many fields of science. In this study we fabricated thin films of the hybrid materials formed as a result of interactions between C_{60} fullerenes and 3-aminopropyltrimethoxysilane (APTMS). The deposition technique was a combination of spin-coating and evaporation methods. Interactions within the films were investigated by means of X-ray photoelectron spectroscopy and near edge X-ray absorption fine structure spectroscopy (NEXAFS). Surface morphology was measured by atomic force microscopy (AFM). We found that there are strong chemical reactions between the nucleophilic nitrogen atoms from APTMS and electrophilic fullerene molecules. Results of NEXAFS investigations suggest that due to direct interactions between APTMS and C_{60} the electronic structure of the fullerene molecules changes while at the same time AFM proved that the C_{60} molecule diameter is not altered.

1. Introduction

Since the discovery of fullerenes in 1985, scientists all over the world have been exploring specific chemical, physical and photophysical properties of these unusual molecules [1]. Due to their unique structure, electronic properties, great chemical and thermal stability fullerenes have been considered as a valuable component of the advanced materials [2]. Thin fullerene based films have potential applications in many fundamental technologies related to coating and surface modification ranging from devices for solar energy conversion, biosensing to advanced nanostructured devices for microelectronics [3–5]. However, the limited solubility of fullerenes in organic solvents imposes the C_{60} modification with other molecules in order to enable its practical application [6]. Since large amount of the covalent fullerene derivatives preserve electronic properties of the parent C_{60} sphere, surface modification with these molecules is of a great interest for the materials science and the semiconductor industry. This may open the possibility of transferring the unique fullerene characteristics to the bulk of the materials [3]. Therefore investigations and understanding of the chemical and physical processes on these systems play a crucial role in order to realize potential future nanoscale applications by controlled manipulation and modification of interfaces [2].

In this article we focused on investigations of the interactions between fullerene C_{60} molecules with 3-aminopropyltrimethoxysilane (APTMS) within the thin films obtained by means of combined spin-coating and evaporation techniques. We decided to use N containing molecule APTMS in order to increase the affinity of the fullerenes to the siloxane matrix [2]. Since C_{60} fullerenes have a tendency to form clusters due to the van der Waals forces between the particular molecules [6], chemical interactions with APTMS matrix are supposed to decrease this phenomenon. Thus, from the detailed analysis of the results obtained in this work we estimated the influence of APTMS on the formation of thin fullerene layers in the evaporation process. We used the combination of the spectroscopic and microscopic methods to investigate C_{60} monolayer growth during the evaporation process from both physical and chemical point of view. We also measured the stability of prepared systems in the ambient conditions.

The paper is organized as follows: based on the X-ray photoelectron spectroscopy (XPS) results we discuss the stability of the thick fullerene films prepared on the APTMS coated substrate and we continue with investigations of the interactions between the ultra-thin fullerene layer and the APTMS film. Next, we present and discuss near edge X-ray absorption fine structure spectroscopy (NEXAFS) results obtained for the samples composed of the C_{60} and the APTMS and we compare it to the data of the pure fullerene layer. At the end of the experimental part we demonstrate noncontact atomic force microscopy (NC-AFM) surface morphology measurements of the pure APTMS film, ultra-thin C_{60} layer on APTMS and thick fullerene layer on the APTMS. Finally, a summary of the relevant conclusions closes the paper.

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2. Experimental

2.1. Methods

X-ray photoelectron spectroscopy measurements were done using SPECS GmbH X-Ray source (Mg Kα 1253.6 eV) and energy analyzer made by Leybold–Heraeus. Structure due to the satellite radiation was subtracted from the spectra before the data fitting [7,8]. The peak intensities were acquired after Shirley background removal [9]. Corrections for the energy shift were accomplished by assuming 103.5 eV binding energy for the Si 2p peak of the Si^{+4} species [10]. Spectra were decomposed into Gaussian components [11,12].

Near edge X-ray absorption fine structure spectroscopy measurements were performed at the undulator beamline U49/2-PGM2 at Bessy II, Berlin–Adlershof [13,14]. The total electron yield (TEY) signal was measured using the sample current. The total fluorescence yield (TFY) was measured with a fluorescence detector. NEXAFS spectra were normalized to the X-ray intensity I_0, measured on a diode or Au mesh. Decomposition of the NEXAFS spectra was performed using WinXAFS software with asymmetric P–Voigt functions for the resonance peaks and an arctangent for the step function [15].

Noncontact atomic force microscopy measurements were conducted by Veeco CPII at room temperature. Phosphorus doped silicon cantilevers (model MPP-11123-10) with resonant frequency of about 275 kHz and approximate spring constant of 48 N/m were used. The back side of the cantilevers were covered by 50 nm of aluminum. The nominal tip curvature of the used cantilevers was less than 8 nm.

2.2. Sample preparation

2.2.1. Materials and substrates

In this work we used C_{60} (99,5%) and APTMS (97%) obtained from Sigma-Aldrich. We employed two types of substrates: Mo and p-type Si(001). As the APTMS builds a silica matrix, in the initial phase of the experiments this substance was deposited on the Mo surface in order to estimate feasibility of the coating process. We assumed that an evidence of APTMS deposition on the Si(001) substrate may be confused with presence of the SiO_2 native oxide while XPS technique is utilized. The high-quality samples obtained on the Mo substrate allowed us to perform XPS and NEXAFS investigations. Following the experiments on the Mo substrate we switched to a more appropriate Si(001) surface.

2.2.2. Sample preparation

In Fig. 1 we present the schemes of all the investigated samples. After ultrasonification in isopropanol and acetone for 5 min, the substrates were dried in a pure nitrogen stream. APTMS was deposited by means of the spin-coating technique at a speed of 6000 rpm for 1 min in the ambient conditions. The fullerene molecules were deposited on the APTMS coated substrates by resistive evaporation at a pressure of 1×10^{-5} mbar. The temperature of the resistively heated evaporator was set to 800 °C and the sample substrates were kept at a room temperature. In the experiments we varied the evaporation time in order to obtain different thicknesses of the C_{60} layers ranging from the ultra-thin layer fabricated by 2 min of evaporation (sample *D*), to the thick layers obtained by 10 min of evaporation (samples *B* and *E*). The reference sample *F* was produced by the fullerene powder evaporation onto a Si(001) substrate at a temperature of 800 °C and a pressure of 1×10^{-5} mbar for 40 min. Taking into account, that the probing depth of XPS is roughly 10 nm [16–18], we presume that the thicknesses of the "thick" evaporated fullerene layers are higher than 10 nm. Since the evaporation time required to obtain closed C_{60} layer was shorter for the substrate coated with APTMS (10 min instead of 40 min for uncoated substrate) we conclude that APTMS accelerates deposition of the fullerenes.

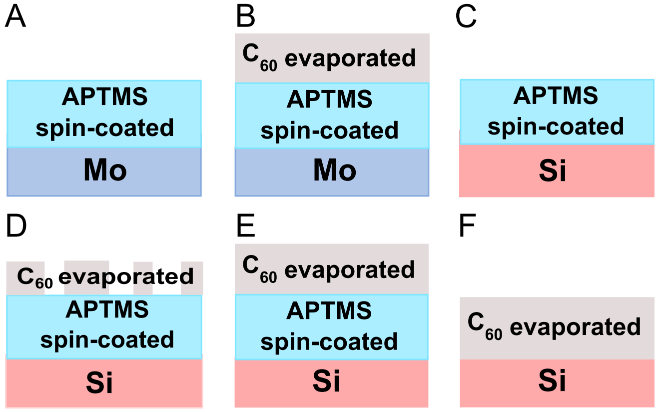

Fig. 1. Schemes of the investigated samples: (A) APTMS spin-coated on the Mo substrate (referred in the text as sample *A*), (B) thick C_{60} layer evaporated on the APTMS spin-coated on the Mo substrate (sample *B*), (C) APTMS spin-coated on the Si substrate (sample *C*), (D) ultra-thin C_{60} layer evaporated on spin-coated APTMS surface on the Si substrate (sample *D*), (E) thick C_{60} layer evaporated on the spin-coated APTMS surface on the Si substrate (sample *E*), (F) thick C_{60} layer evaporated on the Si substrate (sample *F*).

3. Results and discussion

3.1. XPS measurements

Since XPS allows to evaluate the chemical composition of the surface [19] we applied this tool in order to study the C and N chemical states. Additionally, we also performed the analysis of the O and Si core levels. For all measured films quantitative XPS analysis has been done.

3.1.1. Samples deposited on the Mo surface

In this part of the experiment samples *A* (Fig. 2(a–d)) and *B* (Fig. 2(e–h)) were investigated. Sample *B* was investigated twice: first time in situ direct after the C_{60} deposition (Fig. 2h) and second time after 9 months of the storage in the air (Fig. 2(e–g)). The main attempt of these measurements was to investigate the ambient influence on the analyzed films.

After the XPS spectra decomposition, the quantitative analysis of the investigated films was performed. The spectra normalization was achieved by dividing the observed relative peak areas by atomic and instrument sensitivity factors equal to 0.711, 0.296, 0.477 and 0.339 for O, C, N and Si, respectively [19]. Based on the analysis results, the following composition in atomic percent was obtained: C=45.2%, N=10.8%, O=32.1%, Si=11.9% for the samples *A* and C=73.6%, N=2.8%, O=23.7% for the sample *B* after the storage in the air. The stoichiometry of an unhydrolyzed APTMS monomer (excluding H atoms) corresponds to C_6NSiO_3, for the sample *A* the calculated stoichiometry was around $C_{3.8}N_{0.9}SiO_{2.7}$. Taking into account that the "ideal" poly[(aminopropyl)siloxane] polymer has a stoichiometry of $C_3NSiO_{1.5}$ [10] we conclude, that within film *A* the monomers have partially undergone the condensation reactions during the spin-coating and drying process.

Since XPS provides information about the chemical states of the elements within the analyzed surface [25], the qualitative analysis based on the particular peak shifts has been performed. Results of the analysis are reported in Table 1.