SCANNING PROBE MICROSCOPY STUDIES OF FULLERENE C_{60}/POROUS SILICON MULTILAYER STRUCTURES

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The C_{60}/glass, C_{60} /porous Si /Si (C60/PS/Si) thin film structures were prepared and studied by scanning probe microscopy at room temperature. AFM image of the fullerene C_{60} film deposited on glass substrate at room temperature, obtained in non-contact mode shows the dense and regular character of the clusters. Carbon and silicon distributions in the porous part of the C_{60}/PS/Si structure were determined. It was shown that the C_{60} molecules penetrate deep into PS closely to single part of the silicon. Moreover, the EDS analysis shows the presence of oxygen in PS along with the $_{C60}$ molecules.

Keywords: fullerene, porous silicon, scanning probe microscopy.
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1. INTRODUCTION

C_{60} thin films deposited on different substrates have been prepared and extensively studied for a long time since the discovery [1] of C_{60} bucky ball molecules. Today, room temperature solid phase of C_{60} is known as phase centered cubic (fcc) pristine C_{60} [2] or, shortly, fullerite C_{60}. The available vast experimental data on optical and electronic properties of fullerite C_{60} witness that along with emerged band properties, solid state manifestation of C_{60} retain clear-cut molecular fingerprints, such as vibronic transitions and Frenkel excitons [3].

Interpretation of the available numerous experimental data on optical transitions at, below and above band gap remain rather controversial up to now. According to optical absorption and luminescence measurements [4-6], the distance between the occupied (HOMO) and unoccupied (LUMO) states is between 1.5 and 2.7 eV. Such a big uncertainty is largely associated with the overlapping of the spectral features of the molecular and purely band transitions at small values of absorption coefficient.

In the present work scanning probe microscopy (AFM, SEM, EDS) studies of C_{60} thin films on soda lime glass (SLG) substrate and C_{60}/PS/Si multilayer structures, for which the molecular radiative transitions strongly dominate over interband radiative transitions, are studied. X-ray diffraction and Raman spectroscopy analyses are also done for the sake of completeness. The results of the studies can be useful for the interpretation of the available numerous experimental data on optical transitions in these structures.

2. EXPERIMENTAL DETAILS

High purity (99.99%) fullerene powder (C_{60}) was deposited on soda lime glass substrate (C_{60}/SLG) by sublimation technique in a vacuum of 10^{-6} Torr. For comparison, the same fullerene powder was also deposited directly on silicon (C_{60}/Si) and porous silicon (C_{60}/PS/Si) preliminarily fabricated on silicon substrate by anodic etching. The thicknesses of C_{60} films were measured during evaporation by using a deposition controller (Inficon, Leybold) and were in the range of 100-200 nm. PS layers with thickness of 10-20 μm were prepared on p-type Si substrate (with resistivity ρ≈10 Ω.cm) by anodic etching in HF: H_2O solution under the white illumination [7]. The average porosity, i.e. the void fraction in the porous layer was measured by gravimetric technique, using the equation $P = \{(m_1 - m_2) / (m_1 - m_3)\}\ 100\ \%$ [8]. Here m_1 is Si sample mass before the etching, m_2 after etching and m_3 after the removal of the porous layer by rapid dissolution of the completely porous layer in a 3% KOH solution. The porous silicon thickness (d) was determined using the equation $d = (m_1 - m_2) / \rho S$, where ρ is the Si density (2.33 g/cm^3) and S is the etched surface. The average porosity for PS layers and density of pores were found to be 70-75% and 3.4 10^{10} cm^{-2}, respectively.

X- ray diffraction (XRD) analyses of the films were carried out using Bruker D2 Phaser (Germany) diffractometer in θ-2θ scan mode with Ni-filtered CuKα radiation (λ=1.54060 Å) source.

Topography analysis of the films were performed in Smart SPM 1000 AIST NT (Tokyo Instruments, Japan). Cross-section and elemental analyses of the multi-layer structures carried out using Scanning Electron Microscopy SEM S-4800 with EDS system (Hitachi Ltd., Japan).

Raman spectra were measured by Confocal PL/Raman microscope Nanofinder 30-NM01 (Tokyo Instruments, Inc.).

All of the measurements were performed at room temperature.

3. RESULTS AND DISCUSSIONS

XRD patterns of the films did not reveal any noticeable reflexes. A weak reflex around 2 θ~11º (most intensive line of C_{60} with high degree of crystallinity [9]) appears after relatively long time exposure of the samples to *X* - rays. This is caused, in the first place, by low thicknesses of the obtained films. Of course, incomplete crystallization of the films obtained at room temperature contributes as well. However, the results of the detailed Raman

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studies on the films show that the last factor is not decisive.

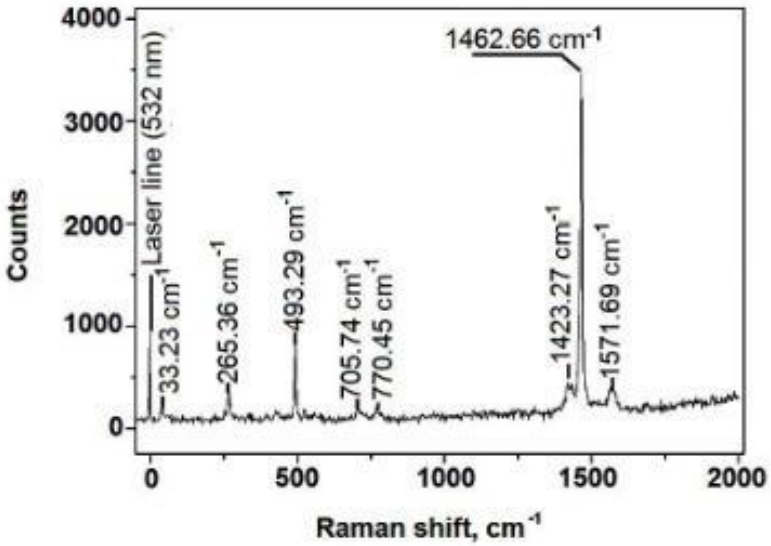

Fig. 1. Raman shift of C60 film on SLG substrate.

The Raman spectrum of a C_{60} film excited with 532 nm laser is shown in Figure 1. Close inspection of the obtained spectrum shows that the last reproduces practically all Raman active modes observed so far on the perfect examples of C_{60} solids [4,8]. These modes lie above 260 cm^{-1} and are intra-molecular in nature. The mode with frequency 33 cm^{-1} is external (inter-molecular) mode and corresponds to librational motions [4].

Figure 2 shows the 3D AFM image of the fullerene C_{60} films deposited on soda lime glass (SLG) substrates at room temperature. The image is obtained in non-contact mode taken over a scale of 4 ×4 μm^2.

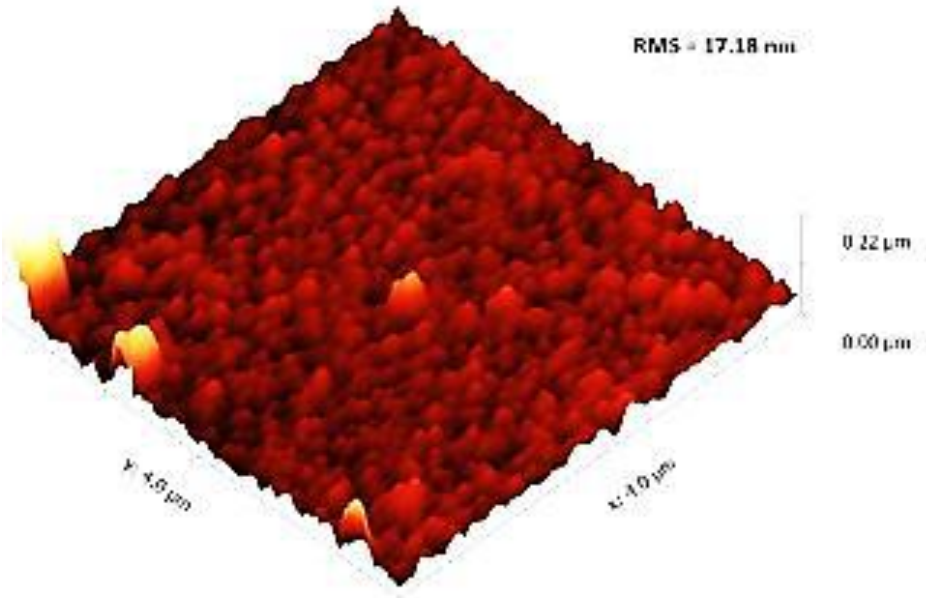

Fig. 2. AFM image of C_{60} film on glass substrate.

Common surface roughness indices, such as root mean square (RMS) roughness and mean roughness (Ra), are 17.8 nm and 17.3 nm, respectively. It is seen that the prepared C60 film is dense and characterized by regularity of the clasters.

In fig. 3, 2D (upper, left hand) and cross-section (upper, right-hand) Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) (lower, left - hand) images of C_{60}/PS/Si multilayer structure is displayed.

Lower right-hand picture shows carbon, silicon and oxygen distributions in the porous part of the structure. As it is clearly seen, the C_{60} molecules penetrate deep into PS closely to single part of the silicon.

Moreover, the EDS analysis shows the presence of oxygen in PS along with the C_{60} molecules.

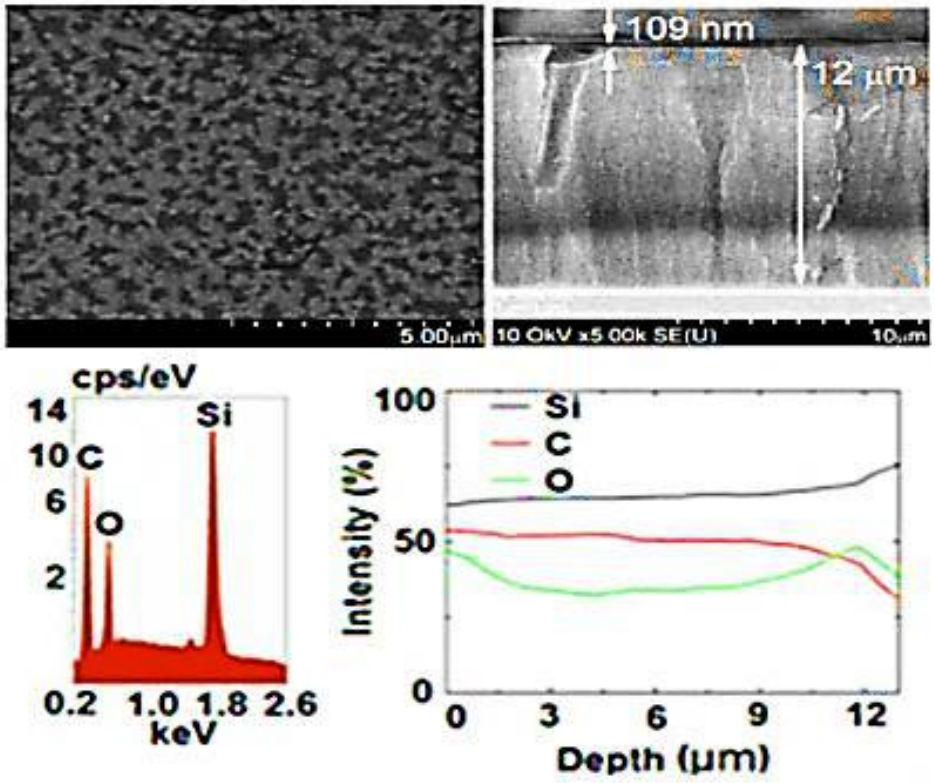

Fig. 3. 2D (upper row, left hand) and cross-section (upper row, right-hand) SEM and EDS (lower row, left hand) and Si, C, O distribution (lower row, right hand) images of C_{60}/PS/Si structure.

4. CONCLUSION

Fullerene C_{60} film on glass is dense and characterized by regularity of the clusters. The Raman spectrum of the film shows that the last reproduces practically all Raman active modes observed so far on the perfect examples of C_{60} solids. C_{60} molecules in the C_{60}/PS/Si multilayer structures penetrate deep into PS closely to single part of the silicon. The EDS analysis shows the presence of oxygen in PS along with the C_{60} molecules.

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