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Analysis of the fundamental absorption edge of the films obtained from the C₆₀ fullerene molecular beam in vacuum and effect of internal mechanical stresses on it

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Abstract. Nanostructures with fullerene C₆₀ were obtained using vacuum sublimation thermal C₆₀ fullerene powder onto unheated substrates made of silicon, mica, silica and coverslip glass. The effect of the structure, composition and mechanical stresses in the films on fundamental absorption, density-of-states tails in them were investigated by Raman spectroscopy, atomic force microscopy, light absorption, electroreflectance modulation spectroscopy and measuring the bend of heterosystems. Ascertained in this work has been the origin of variation observed in literature data concerning the width of the band gap E_g between 1.48 to 2.35 eV and the nature of the fundamental absorption edge in solid C₆₀. This variation is related with decomposition of fullerene molecules caused by the increase in temperature of sublimation. It has been found that C₆₀ in the crystalline state is direct band-gap semiconductor with E_g close to 1.6 eV in the singular point X of the Brillouin zone. The electroreflectance spectra of films and heterosystems bending were used to calculate the E_g dependence on the internal mechanical stresses. The respective coefficient value is equal to $-2.8 \cdot 10^{-10}$ eV/Pa.

Keywords: C₆₀ fullerene film, fundamental absorption, electroreflectance, mechanical stresses.

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1. Introduction

Heteroepitaxial deposition of thin solid films is widely used in modern semiconductor technique and physical researches. Therefore, to find new manufacturing technologies for nanostructures and to identify their physical properties interesting for practical use are rather topical. Due to the unique properties inherent to multi-atomic nanostructures with fullerenes, they attract great attention. Also, they allow modification both during film deposition [1] and due to external effects [2, 3]. Among famous fullerene molecules, C₆₀ is the most symmetrical and stable one. The carbon atoms in it have the covalent type of bonding, while the molecules in respective

crystal exhibit a weak bond corresponding to van der Waals interactions. Development of technologies for the production of fullerenes in the form of film material on various substrates extends the use of nanostructures with fullerenes to various fields of science and nanotechnology, as well as for practical use. Heterostructures based on them are used for solar cells [4, 5] and sensors of physical quantities [6]. Films with C₆₀ fullerenes are promising for applications in biomedicine, robotics, and as protective coatings [7].

Electronic and optical properties of semiconductor are determined by its band structure (a band gap E_g and the type of electronic transitions in it). Up to date, it is not practically ascertained what is the real width of the

band gap in crystalline C₆₀. The data obtained using various methods (optical absorbance, ellipsometry, photoconductivity, microwave conductivity, electron energy loss spectroscopy, surface photovoltaic spectroscopy and photoemission) show a large spread of its value from 1.5 up to 2.35 eV [8], for instance, shown in [9] is the value $E_g = 1.47$ eV.

The discriminating feature of the heterosystems is the presence of internal stresses in them. They arise from the mismatch of lattice parameters and thermal expansion coefficients of the film and substrate, give rise to technological defects at the interface, and change the band structure of semiconductor. Relaxation of internal mechanical stresses in devices reduces their stability [10]. The objective of this work was to study the fundamental absorption of C₆₀ films with different methods and the effect of internal mechanical stresses on it.

2. Experiment

Low temperature sublimation C₆₀ (350 °C) simplifies the process of manufacturing the solid-state fullerene heterosystems. The fullerene films were deposited on various non-heated substrates (silicon, mica, silica, glass coverslip) by evaporation of microcrystalline C₆₀ powder (purity 99.9 %) in vacuum at the pressure of 10⁻⁴ Pa from an effusion tantalum cell at the temperature of 650 to 800 K [1]. The thickness of films was 0.1 to 2 μm. All substrates had a smooth and flat surface. Substrate of silicon was prepared by standard industrial processing with finish chemical polishing. Mica substrates with natural surface were prepared by cleavage. The surface of the silica substrate was mechanically polished. The substrate and film surfaces nanomorphology were studied using atomic force microscopy with a Nanoscope III-a operating in the periodical mode. It is known that even for films of atomic semiconductors the growth rate strongly influences on their structure, internal stresses, optical and electronic properties [11]. Stepped disposition of substrates in vacuum camera enabled us to obtain a single technological cycle of the film at different rates of growth (10 to 500 nm/min) and change their physical properties [7].

To analyze the film composition and fundamental absorption, as well as internal mechanical stresses in the films, we used a complex of experimental methods. It included measurements of Raman scattering, transmission and reflection of light, modulation spectroscopy electroreflectance and the bending radius of heterosystems. To excite Raman spectra, an Ar⁺-laser with the emission wavelengths 514.5 nm was used.

Study of the electron band structure by using the modulation spectroscopy method should help in understanding the nature and mechanism of light absorption of solid C₆₀. A feature of the electroreflectance method is its high resolution, appearance of the signal only at the direct transitions in critical points of the Brillouin zone and its disappearance at some distance from the critical point. The method provides information on the band

structure of semiconductor, its electronic and optical properties, structural perfection and internal mechanical stresses in films and interfaces film-substrate. Note that there is no data in the literature on electroreflectance of fullerenes. To study heterosystems with fullerenes, this modulation method was used for the first time. The measurements were performed in silica electrolytic cell with 0.1N KCl water solution at room temperature. The band gap E_g and parameter of spectral broadening Γ were determined using the three-point method by Aspnes [12]. The value of Γ characterizes the quality of the film surface.

The magnitude and sign of the internal stress in the films were studied by measuring the heterosystem bending recorded on the Talesurf-4 profilograph by using the Stoney formula [13]:

$$\sigma = Ed^2/[6Rt(1 - \nu)], \quad (1)$$

where R is the radius of heterostructure curvature, E and ν – the Young modulus and Poisson's ratio of the substrate, d and t are the substrate and film thicknesses, respectively.

3. Results and discussion

Depending on the conditions for condensation of the C₆₀ molecular beam onto a substrate, the film was prepared with a different crystal structure and composition: polycrystalline fullerite C₆₀, composite (C₆₀:a-C, a-C:C₆₀) and amorphous a-C film not containing fullerenes. The surface of fullerite films was smooth, with uniform arrangement of the molecules on it (Fig. 1a). Raman spectra contain vibration modes with symmetry H_g, A_g, and H_g at frequencies 1425, 1470 and 1575 cm⁻¹, respectively (Fig. 1b).

According to [14], C₆₀ carbon molecules form a molecular crystal, and the new form of C₆₀ carbon crystal has a new semiconductor material with a direct band gap. $E_g = 1.6$ eV within the region E_0 ($h_g - t_{1u}$) transition and near 2 eV higher energy transition ($h_g - t_{2u}$). The top of the valence band and bottom of the conduction one are located at the same point X of the Brillouin zone. The signal of electroreflectance is also present only for direct transitions. From the electroreflectance spectra of the C₆₀ film on a silicon substrate (Fig. 2a), we have $E_g = 1.65$ eV for ($h_g - t_{1u}$) transition and about 2.1 eV for ($h_g - t_{2u}$) transition. These data coincide with the value E_g obtained from absorption spectra of the films on transparent substrates. The C₆₀ fullerene band gap depends on the presence of mechanical stresses. Regardless of the conditions for obtaining the films, they were always present on the convex side of the substrate. It means that in films the compression stresses occur and in the substrate – stretching ones [13]. Fig. 2b shows the dependence E_g in films C₆₀ determined from the spectra of electroreflectance and fundamental absorption edge for the E_0 transition on the stresses σ : $dE_g/d\sigma = -2.8 \cdot 10^{-10}$ eV/Pa.

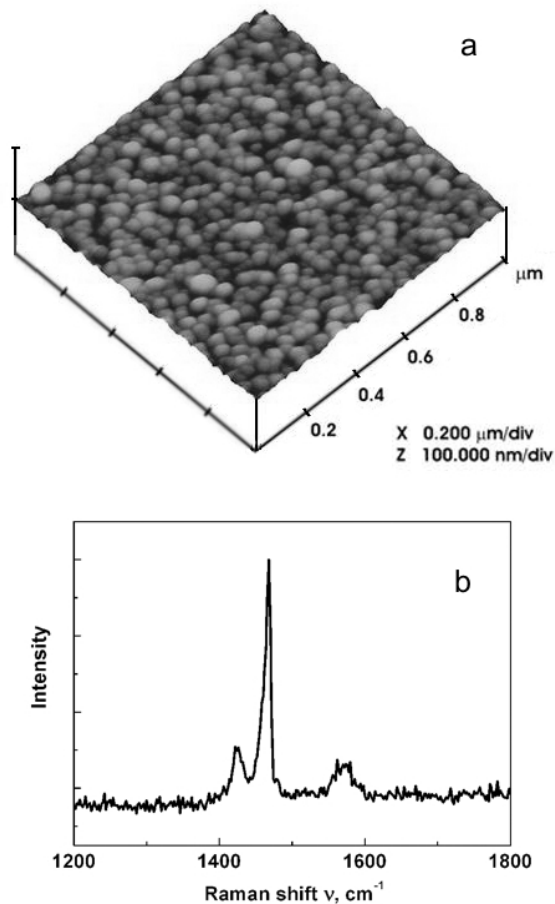


Fig. 1. Image of the surface (a) and Raman spectra (b) of the fullerene C_{60} films on silicon.

A large spectral broadening in the electroreflectance spectra of C_{60} films ($\Gamma = 100 \dots 150$ meV) corresponds to their polycrystalline structure. The value of Γ characterized the scattering of light excited charge carriers on the structural defects, which leads to a broadening of the fundamental absorption edge due to the presence of tails in the density of states within the band gap of the film. In classical spectroscopy, they arise in the form of an exponential dependence at the fundamental absorption edge when the photon energy is less than E_g and determined by the value of the characteristic energy $\Delta = dE/d \ln k$, where k is the coefficient of light absorption. In polycrystalline C_{60} films, the Δ value is tens of millielectronvolts, and it is independent of their thickness 0.1 to 2 μm , which coincides with the data of [15] to C_{60} polycrystalline films with a thickness 1.3 to 8.5 μm , obtained using the similar method. It means that the fundamental absorption has a bulk property of C_{60} films without surface or interface. The authors of [15] believe that the fundamental absorption edge of polycrystalline films of C_{60} is indirect, and the absorption edge is identical to that of the single-crystal C_{60} sample with the size of 1 mm^3 ($\Delta = 43$ meV). The spectral dependences of $k^2(E)$

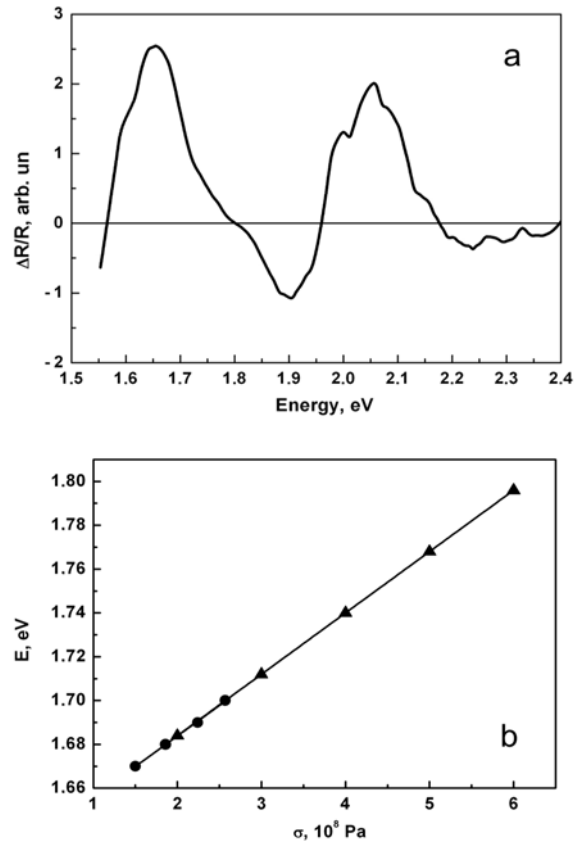


Fig. 2. (a) Spectrum of electroreflectance in C_{60} films on silicon, (b) dependence of the band gap E_g on internal mechanical stresses σ in C_{60} films on silicon (\blacktriangle) and glass (\bullet) substrates for E_0 ($h_g - t_{1u}$) transition.

and $\ln k(E)$ for C_{60} films in the range of the following direct transition ($h_g - t_{1u}$) are shown in Fig. 3. The films have $E_g = 2.24$ eV (Fig. 3a) and the parameter $\Delta = 82$ eV (Fig. 3b).

With increasing the growth rate (sublimation temperature of fullerenes) morphology, composition and crystal structure of the films are changed. The surface of the film was not smooth and inhomogeneous (Fig. 4a). In the Raman spectrum, instead of a strong signal from the pentagons at 1470 cm^{-1} , a very weak signal appeared on broad background photoluminescence (Fig. 4b). Instead of narrow lines at 1425 and 1575 cm^{-1} , recorded were broad bands with the maxima at 1380 and 1600 cm^{-1} . This fact indicates a change in composition and structural perfection of the films with occurring diamond and graphite-amorphous phases in them. Their appearance is caused by the collapse of the C_{60} molecules on the surface of the substrate [1]. Significant changes have also occurred at the edge of the fundamental absorption inherent to composite carbon films. The signal of electroreflectance in them is absent, which is typical for amorphous material [1]. Spectral distribution of the light absorption coefficient and its logarithmic dependence are also changed. The films on

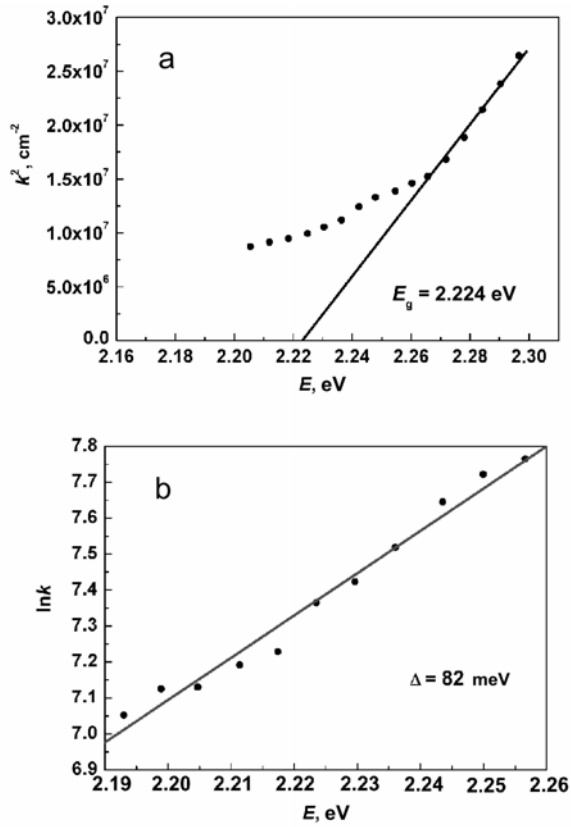


Fig. 3. Spectral dependence of k^2 (a) and $\ln k$ (b) for a-C:C₆₀ films on mica in the range of the ($h_g - t_{2u}$) transition.

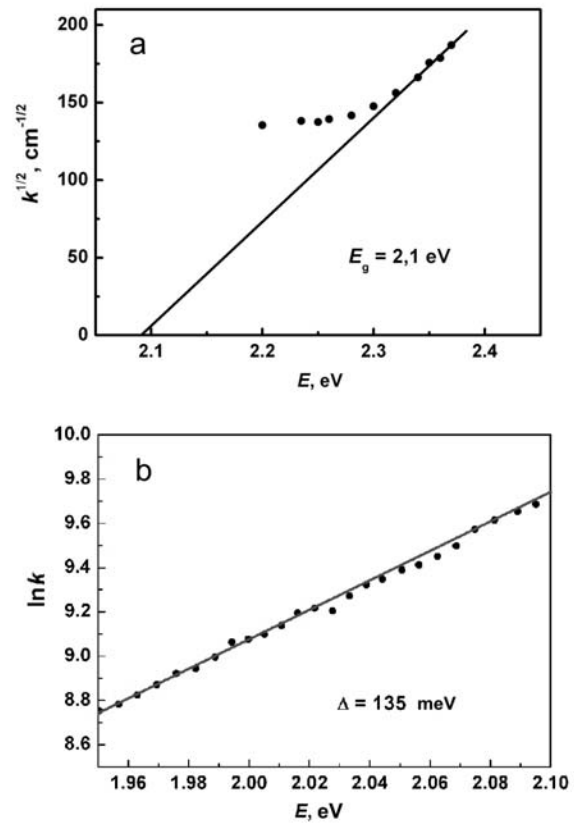


Fig. 5. Spectral dependence of $k^{1/2}$ (a) and $\ln k$ (b) for a-C:C₆₀ films on silica in the range of ($h_g - t_{2u}$) transition.

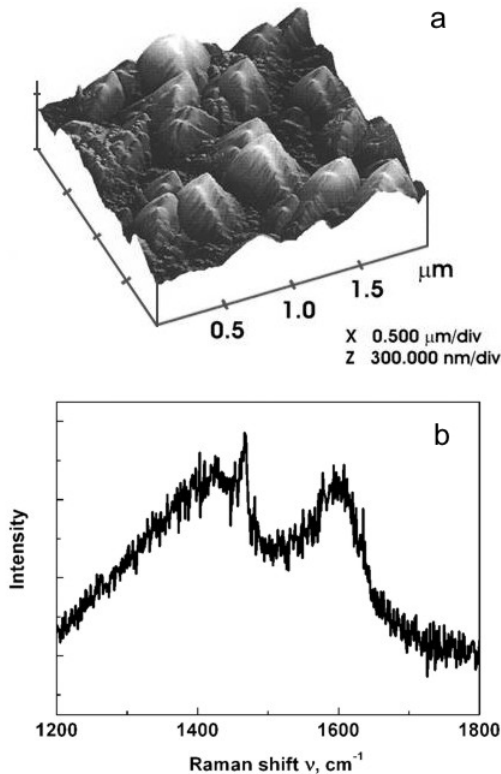


Fig. 4. Image of the surface (a) and Raman spectra (b) of the composite a-C:C₆₀ film on silicon.

the polished silica have $E_g = 2.1$ eV (Fig. 5a) and the parameter $\Delta = 135$ meV (Fig. 5b). Since the maximum value of Δ for any amorphous material does not exceed 140 meV [16], a large Δ parameter for our films confirms their amorphous structure.

For the individual C₆₀ molecule, there is an internal transition at the energy 1.6 eV. It is forbidden for C₆₀ in the solid state [17]. Due to interaction of the molecules with each other, in fullerene crystals and films this prohibition is removed, and in that spectral region the C₆₀ films also absorb light. The authors [17] explain the fundamental absorption edge in molecular crystals by indirect Frenkel excitons within the range 1.5 to 2 eV, while the authors of [9] – by an internal transition in C₆₀, calling it as the mobility edge and defining it as the indirect one. The edge of the intrinsic light absorption in C₆₀ crystal and films the authors of [14] also determine it as indirect.

4. Conclusion

The results of comprehensive experimental investigation of the films prepared using the molecular beam C₆₀ falling in vacuum onto various substrates showed strong influence of the preparation process conditions on composition, structure, optical properties, internal mechanical stresses of films and enabled to draw the following conclusions. Uniquely set are causes of variation in the

literature data on the band gap magnitude in C₆₀ films and the nature of fundamental absorption edge in them. The polycrystalline semiconductor films of C₆₀ have a direct edge of the fundamental absorption in the spectral region near 1.65 eV. Their band gap increases with stress by a factor $dE_g/dP = -2.8 \cdot 10^{-10}$ eV/Pa. The mechanical stress in amorphous films decreases, and their absorption edge is near 2.2 eV. High-energy direct transitions in C₆₀ polycrystalline films have been also registered in this spectral region.

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