Analysis of the fundamental absorption edge of the films obtained from the C$_{60}$ fullerene molecular beam in vacuum and effect of internal mechanical stresses on it

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Abstract. Nanostructures with fullerene C$_{60}$ were obtained using vacuum sublimation thermal C$_{60}$ 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 Ramana 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 C$_{60}$. This variation is related with decomposition of fullerene molecules caused by the increase in temperature of sublimation. It has been found that C$_{60}$ 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 $-2.8 \times 10^{-10}$ eV/Pa.

Keywords: C$_{60}$ fullerene film, fundamental absorption, electroreflectance, mechanical stresses.

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, C$_{60}$ 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 C$_{60}$ 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 ascertainment what is the real width of the
band gap in crystalline C_{60}. 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 stresses in films and interfaces film-substrate. Note that there is no data in the literature on photoconductivity of fullerene. To study heterosystems with fullerene, 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 $\Gamma$ were determined using the three-point method by Aspnes [12]. The value of $\Gamma$ 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]:

$$
\sigma = \frac{E_d \nu}{6 R_t} (1 - \nu),
$$

where $R$ is the radius of heterostructure curvature, $E$ and $\nu$ – 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 C_{60} molecular beam onto a substrate, the film was prepared with a different crystal structure and composition: poly-crystalline fullerite C_{60}, composite (C_{60}:a-C, a-C:C_{60}) 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 $\Gamma_{5}$, $\Gamma_{4}$, and $\Gamma_{8}$ at frequencies 1425, 1470 and 1575 cm$^{-1}$, respectively (Fig. 1b).

According to [14], C_{60} carbon molecules form a molecular crystal, and the new form of C_{60} carbon crystal has a new semiconductor material with a direct band gap. $E_g = 1.6$ eV within the region $E_0$ ($h\nu = 1.0\mu m$) transition and near 2 eV higher energy transition ($h\nu = 1.2\mu m$). 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 C_{60} film on a silicon substrate (Fig. 2a), we have $E_g = 1.65$ eV for ($h\nu = 1.0\mu m$) transition and about 2.1 eV for ($h\nu = 1.2\mu m$) transition. These data coincide with the value $E_g$ obtained from absorption spectra of the films on transparent substrates. The C_{60} 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 C_{60} determined from the spectra of electroreflectance and fundamental absorption edge for the $E_0$ transition on the stresses $\sigma$: $dE_g/\sigma = – 2.8 \times 10^{-10}$ eV/Pa.
Fig. 1. Image of the surface (a) and Raman spectra (b) of the fullerene C₆₀ films on silicon.

A large spectral broadening in the electroreflectance spectra of C₆₀ films ($\Gamma = 100 \ldots 150$ meV) corresponds to their polycrystalline structure. The value of $\Gamma$ 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 C₆₀ films, the $\Delta$ 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 C₆₀ 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 C₆₀ films without surface or interface. The authors of [15] believe that the fundamental absorption edge of polycrystalline films of C₆₀ is indirect, and the absorption edge is identical to that of the single-crystal C₆₀ sample with the size of 1 mm² ($\Delta = 43$ meV). The spectral dependences of $k^2(E)$ and $\ln(E)$ for C₆₀ films in the range of the following direct transition (h_g – t₁u) 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 C₆₀ 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:C$_{60}$ films on mica in the range of the $(h_g - t_{2u})$ transition.

Fig. 4. Image of the surface (a) and Raman spectra (b) of the composite a-C:C$_{60}$ film on silicon.

Fig. 5. Spectral dependence of $k^{1/2}$ (a) and $\ln k$ (b) for a-C:C$_{60}$ films on silica in the range of $(h_g - t_{2u})$ transition.

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

For the individual C$_{60}$ molecule, there is an internal transition at the energy 1.6 eV. It is forbidden for C$_{60}$ 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 C$_{60}$ 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 C$_{60}$, calling it as the mobility edge and defining it as the indirect one. The edge of the intrinsic light absorption in C$_{60}$ 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 C$_{60}$ 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 C_{60} films and the nature of fundamental absorption edge in them. The polycrystalline semiconductor films of C_{60} 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 \( \frac{dE_g}{dP} = -2.8 \times 10^{-10} \text{ eV/Pa} \). The mechanical stress in amorphous films decreases, and their absorption edge is near 2.2 eV. High-energy direct transitions in C_{60} polycrystalline films have also been registered in this spectral region.

References