

Effect of ultrasound treatment on the optical properties of C₆₀ fullerene films

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ABSTRACT

C₆₀ fullerene films on silicon substrates are investigated by luminescence and multi-angle-of-incidence (MAI) ellipsometry. The ultrasonic treatment decreases the integral intensity and modifies the photoluminescence spectrum shape. The optical properties of C₆₀ fullerene films are shown to be well described within a two-layer model, a bulk fullerene layer and a surface film. It is found that the ultrasonic treatment mainly affect the optical constants of the surface layer. The change of the film optical properties is caused by the decrease of the defect concentration due to the ultrasonic treatment.

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1. Introduction

In the last time the investigation of thin films, particularly, the films of nanoparticles such as fullerenes and carbon nanotubes, attract great attention of scientist in the context of using them in novel electronic devices [1,2]. At the same time, preparation of such defect-free films is difficult [3]. The traditional methods of defect elimination after the film formation, like annealing or other treatments, are not always usable because the heating can lead to modifications of other physical properties [4]. There is a limited number of works devoted to the defect content modification in bulk semiconductors by ultrasonic treatment (UT) [5]. The aim of this work is therefore to study of UT influence on the optical properties of C₆₀ fullerene thin films.

2. Experiment

The C₆₀ films are grown on Si substrates at 20 °C by thermal vacuum deposition. The pressure in the vacuum chamber is about 10^{−5} Torr. The temperature in the evaporator with C₆₀ powder is 450 °C. The deposition rate of C₆₀ is about 10 nm/s. The deposited film thickness is controlled by calibrated optical sensor. The 335 nm thick C₆₀ films are obtained.

Four samples are studied. The first is the untreated C₆₀ sample. The second one is subjected to a phototransformation described in [6,7]. The third sample is exposed to ultrasound and the fourth is treated by ultrasound after the phototransformation process.

The experimental setup for UT is shown in the inset to Fig. 1. The piezoelectric transducer is used for generation of the acoustical oscillations in the studied structures. The acoustical contact between the transducer and silicon substrate is fulfilled. As a result,

we have obtained the acoustical vibration of C₆₀ film with silicon substrate. The UT is performed at 547 kHz for 6 h. The ultrasound power density is 1 W/cm². The C₆₀ film temperature during the UT treatment is 25 ± 1 °C. The film phototransformation is realized by a 8 W xenon lamp irradiation for 12 h.

Luminescence is excited by a 488 nm LGN-402 Ar⁺ laser. The power density of the excitation was 6 W/cm². The spectra are measured at liquid nitrogen temperature. The intensities in the presented spectra are proportional to the quantum number per the spectral interval units. The spectral sensitivity of the setup is taken into account. The spectral width of the slit does not exceed 7 nm.

The optical constants such as the refraction index n , the absorption coefficient k , the real $\text{Re } \varepsilon \equiv \varepsilon_1 = n^2 - k^2$, and the imaginary $\text{Im } \varepsilon \equiv \varepsilon_2 = 2nk$ are obtained by multi-angle-of-incidence (MAI) ellipsometry. The measurements are performed using LEF-3M null-ellipsometer with a 632.8 nm He–Ne laser as a light source. The n , k , and the layer thickness d are found to be fit the experimental curves of $\psi(\varphi)$ and $\Delta(\varphi)$ ellipsometric angles to the theoretical ones using the program of quadratic objective function minimization [8].

3. Results and discussion

Two wide infrared bands near 1.5 and 1.69 eV can be observed in the photoluminescence spectra (PL) (Fig. 1). This is in agreement with the results of other authors [9]. The intensities of the bands are approximately equal at room temperature whereas the high-energy intensity dominates in the spectrum at 85 K.

The 1.69 eV peak of the radiative recombination is caused by the 0'–0 transition from the localized state related to the dimer 'X-trap' [10,11]. The agreement is absent in case of the 1.5 eV peak. On one hand, the peak is attributed to the emission of different 'X-centers' as a consequence of the transitions from the localized states of traps, connected with different types of the crystal lattice

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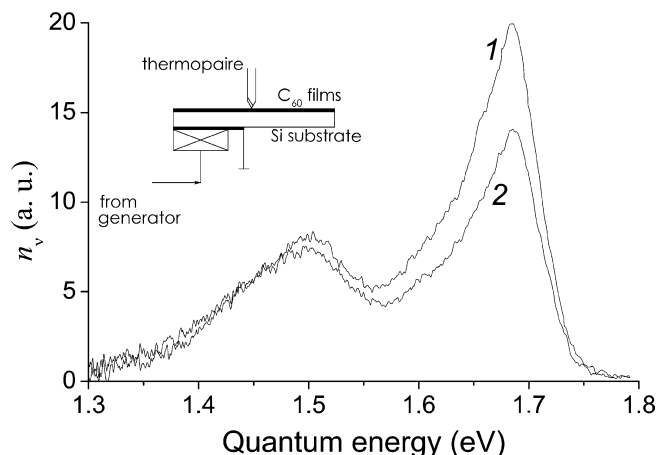


Fig. 1. PL spectra of initial sample (1) and the sample after UT (2). The experimental setup for ultrasound treatment is shown in the inset.

defects, to the phonon levels of the odd symmetry of basic electronic A_g state (Herzberg–Teller transitions) [12,13]. In other works [10,11] these peaks are considered as the result of a transitions from the localized state of dimer traps to the different phonon bands of the even symmetry of the ground state. It should be noted that the intensity ratio of these peaks substantially depends on the conditions for the C_{60} fullerene film preparation [14].

The UT of C_{60} fullerene films on the Si substrate decreases the integral intensity of PL for about 20% (Fig. 2). It should be noted that the UT affects the 1.5 eV band intensity much less essentially as compared to the 1.69 eV band. A change in the 1.69 eV peak intensity, as a result of the ultrasound exposure, can be explained by a degradation of the localized state concentration.

The obvious asymmetry of the 1.69 eV band can be explained by the depth heterogeneity of the film optical properties [3]. It is shown by the ellipsometric measurements (Fig. 3), that the film optical parameters are well described within the two-layer model: the bulk layer with $n_2 = 2.10 \pm 0.05$, $k_2 = 0.04 \pm 0.01$, $d_2 = 310 \pm 30$ nm bordering the substrate and the 25 ± 2 nm thick surface layer with $n_1 = 2.70 \pm 0.05$, $k_1 = 0.0 \pm 0.01$ (Table 1). The optical constants of C_{60} fullerene films ($n = 2.0$ – 2.1) presented by other authors [15,16] are in agreement with the data for our samples. A high value of $n = 2.7$ for the surface layer of the C_{60} fullerene film may be due to a quantity of damaged C_{60} molecules, oxygen atoms and other defects of the film. Thus, the greatest changes of the opti-

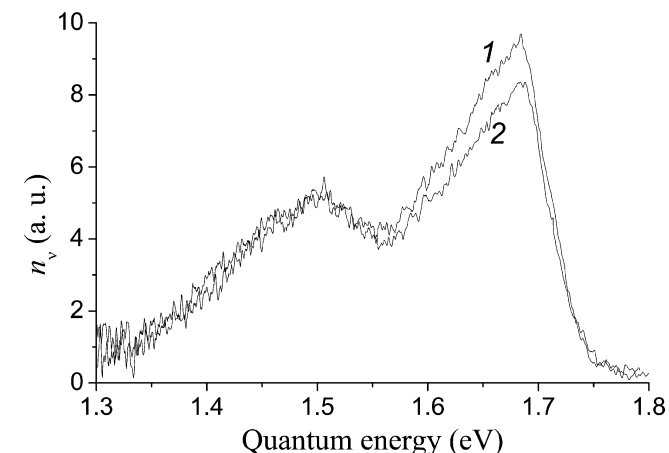


Fig. 2. PL spectra of the phototransformed C_{60} fullerenes before (1) and after UT (2). The intensities are normalized at the 1.5 eV band.

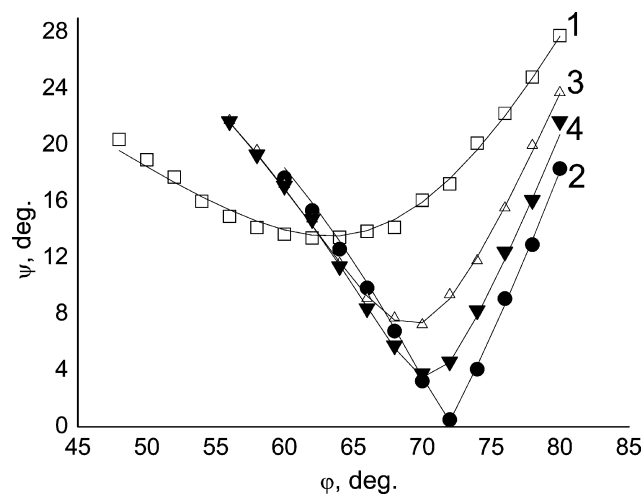


Fig. 3. Angle dependencies $\psi(\phi)$ for the initial C_{60} fullerene/Si sample (1), phototransformed one (2), the one exposed to ultrasound (3) and the sample treated by ultrasound after the phototransformation (4). The symbols are the experiment, the lines are the theoretical curves fitted to the experimental results by minimization of quadratic objective function [8].

Table 1

The calculated values of parameters for C_{60} fullerenes films. n_1 , k_1 , d_1 are parameters for the surface layer and n_2 , k_2 , d_2 correspond to the bulk C_{60} film.

Sample	n_1	k_1	d_1 (nm)	n_2	k_2	d_2 (nm)
1 (init.)	2.70	0.0	25.0	2.10	0.040	310
2 (phototr.)	1.88	0.0	25.0	2.13	0.054	310
3 (UT)	1.67	0.0	25.0	2.08	0.059	310
4 (phototr. + UT)	1.69	0.0	25.0	2.09	0.058	310

cal constants are observed for the surface layer, where the defect concentration is much higher than that in the bulk fullerene C_{60} film.

Ultraviolet irradiation of the C_{60} fullerene films leads to their phototransformation and optical property modification [6,7]. The irradiation of the studied structures caused the reduction of the refractive index value of the surface layer from 2.7 to 1.88. The optical constants n and k for the bulk layer are not essentially changed.

After the phototransformation of the sample, the PL intensity of both bands is reduced about twice. At the same time the 1.69 eV peak asymmetry is enhanced. The luminescence efficiency degradation can be explained by a decrease of the defects being the radiative recombination centers.

Effect of the UT on the luminescence spectrum and efficiency of the phototransformed sample is almost not observed, though the tendency for redistribution of the band intensities also manifests itself. At the same time the refractive index of the surface layer is little reduced.

4. Conclusion

Two bands with the peaks at 1.5 and 1.69 eV are observed in the PL spectrum of the C_{60} fullerene films on a Si surfaces. The treatment by ultrasound reduces the PL efficiency. The UT affects mainly the high-energy spectral band and changes the refractive index of the surface layer of C_{60} fullerene film. At the same time the optical parameters of the rest of film are not modified essentially. The modification of the film optical properties can be due to decrease of the defects caused by UT.

So, the results show a technical possibility to modify the optical constants and luminescent properties of C_{60} fullerene films by ultrasound, which is important for using them in novel electron and optoelectronic devices.

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