

# The effect of temperature on the properties of graphene oxide langmuir films

E Seliverstova<sup>1</sup>, N Ibrayev, R Dzhanabekova, V Gladkova

Institute of Molecular Nanophotonics, Karaganda 100028, Kazakhstan

E-mail: genia\_sv@mail.ru

**Abstract.** The effect of temperature on the optical properties and structure of graphene oxide langmuir films was studied. It is shown that the decrease of optical density of the films in the absorption band of graphene oxide take place when the film was heated above 100 °C. Increasing the temperature of the films over 200 °C leads to the growth of its optical density. As it was shown with the scanning electron microscopy the structure of graphene oxide films annealed at different temperatures is practically unchanged. Measured the Raman spectra show that in the films there are a partial reducing of disordered and high-defective graphene oxide LB films occurs under heat treatment. This process accompanied by ordering of amorphous sp<sup>3</sup> clusters and its transition in sp<sup>2</sup>-bonded carbon clusters.

## 1. Introduction

Many studies demonstrate that the optical and structural properties of graphene and coatings based on it are not only depending on acidity of medium but on its temperature too. For example, in the work of [1] it has shown that high temperature and chemical treatment of graphene films is not only leads to a decrease in their resistance, but also to increase of their transparency. As it was demonstrated in works of [2, 3] this is due to partial reduction of graphene oxide. Since LB film based on graphene will be subjected to not only of light but also to heat exposure in solar cells, it is necessary to examine how these factors will affect their optical and structural properties. Unfortunately, at present there are practically no studies on the effect of temperature on the structural and optical properties of graphene oxide Langmuir-Blodgett (LB) films SLGO.

## 2. Experiment

Single layer graphene oxide was used for dispersion preparation (SLGO) (Cheaptubes, USA). The suspensions of graphene oxide were prepared in dimethyl formamide (DMF, Sigma Aldrich) by ultrasonication. and used without purification. Solid films were obtained by Langmuir–Blodgett (LB) technology. Monolayers were formed on the surface of the subphase by spreading of solution in the LB through (KSV NIMA Medium). The deionized water was cleaned by AquaMax and was used as subphase. The resistivity of the deionized water was equal to 18.2 MΩ·cm<sup>-1</sup>. The surface tension of water was equal to 72.8 mN/m at pH=5.6 and temperature 22 °C.

Obtained films were heated to various temperatures from 50 to 250 °C in the muffle furnace during 1 hour/ Temperature was changed in increments of 25 °C. Absorbance and transmittance of LB films after annealing was measured with using of Cary-300 spectrophotometer (Agilent). Measurements of

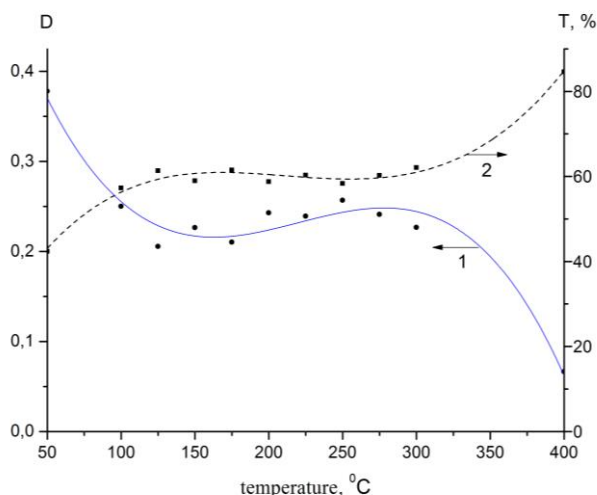
<sup>1</sup> To whom any correspondence should be addressed.



Raman spectra were carried out with the spectrometer Solver Spectrum under laser excitation with wavelength of generation equal to 473 nm in the National Nanotechnology Laboratory of the Al-Farabi Kazakh National University

### 3. Results and discussion

The dependence of optical density and transmission via temperature of graphene oxide LB films is shown on the Figure 1.



**Figure 1.** Dependence of optical density (curve 1) and transmittance (curve 2) of SLGO LB film via temperature ( $\lambda_{\text{reg}} = 226$  nm).

As it can be seen, when the SLGO LB films was heated up to 100 °C there is a twice reduction of graphene oxide absorption. Further annealing of films leads to the decreasing of D values by 10 – 15% for every 25 °C. At temperatures above 200 °C the changes in optical density was not registered. In this case, as it was seen with the naked eye, the color of the film was changed from dark brown to black and gray, indicating on partial reduction of graphene oxide to graphene. With this process a slight increase in the optical density of the film in the temperature range from 225 to 275 °C is connected, apparently.

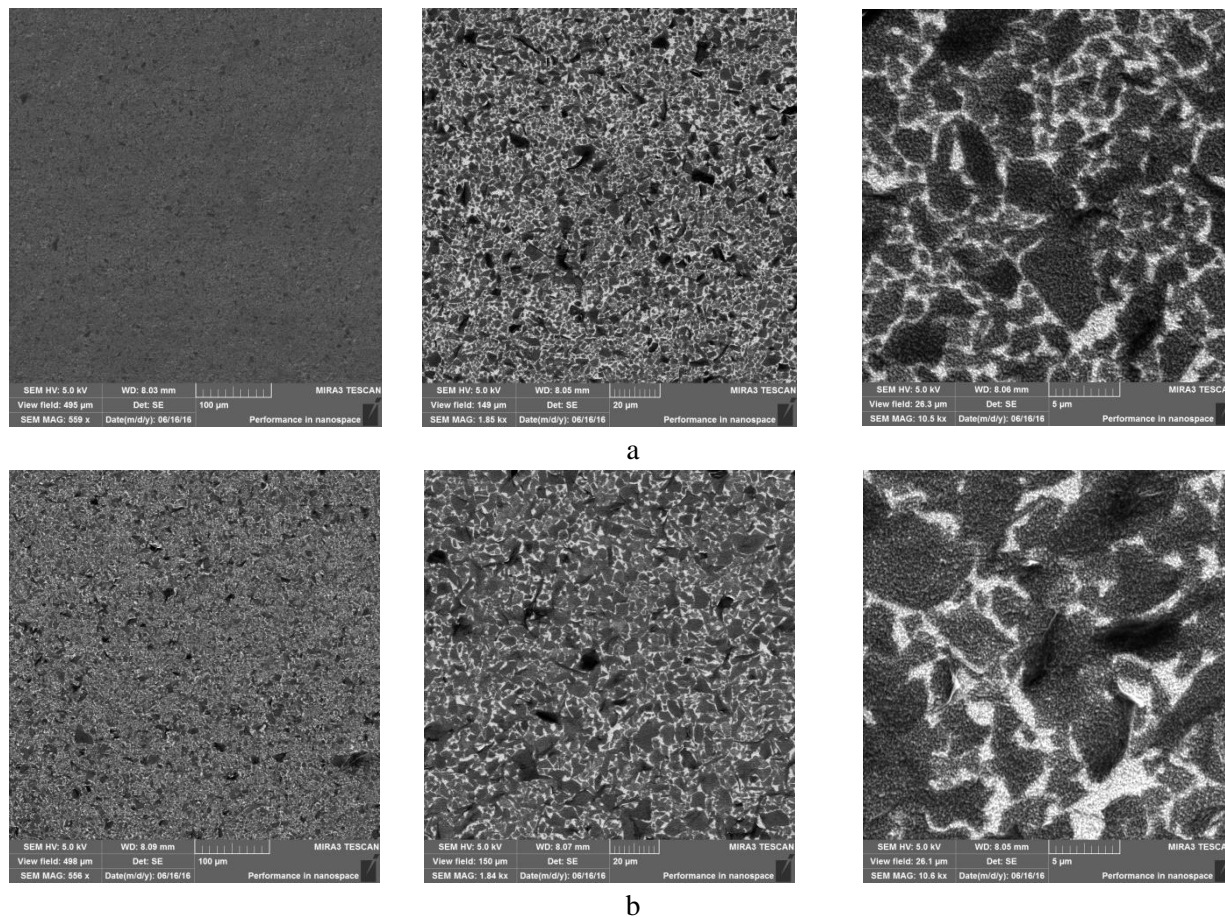
Film heating up to 400 °C leads to a significant decrease in the absorbance of SLGO, which is associated with the destruction of the LB film. The transmittance of the film behaves in the opposite way. Thus, the annealing improves the transparency of the film from 40 up to 60%.

SEM studies reveals that the structure of film SLGO heated at different temperatures is almost constant (Figure 2).

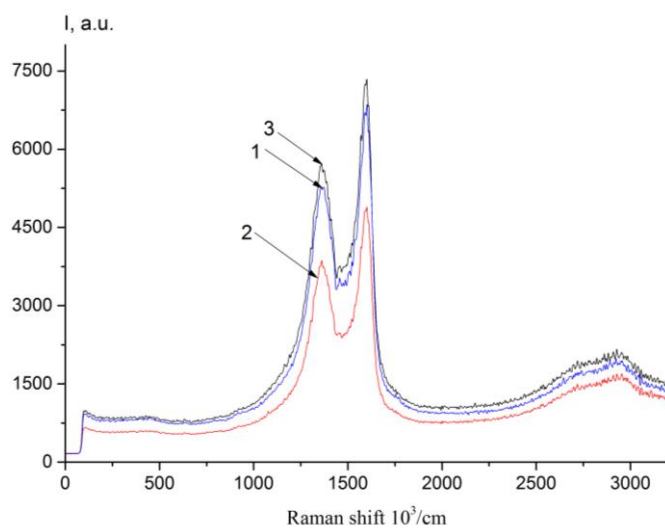
In order to explain the decrease in absorbance of LB films of graphene oxide the Raman spectra were recorded. The measurement results are shown in Figure 3 and Table 1.

**Table 1.** Position and intensity of Raman bands of SLGO in LB films after heating.

Temperature, °C	D, $\text{cm}^{-1}$	I, a.u.	G, $\text{cm}^{-1}$	I, a.u.	$I_D/I_G$	2D, $\text{cm}^{-1}$	I, a.u.	$I_{2D}/I_G$
0	1360	5279	1602	6979	0,76	2740	1767	0,25
125	1360	3900	1602	4920	0,78	2720	1469	0,29
200	1360	5751	1602	7372	0,79	2720	1916	0,26



**Figure 2.** SEM images of SLGO LB films after heating at temperature of: (a) 50 °C, (b) 200 °C.



**Figure 3.** Raman spectra of SLGO LB films before (1) and after heating at temperature of: 2 – 125 °C, 3 – 200 °C.

There are several bands can be clearly distinguished in the Raman spectra of the synthesized LB films. As a rule, the most informative are G and D-bands [4, 5]. The table show that the G-band of graphene oxide is appears at  $1602\text{ cm}^{-1}$ . This position is shifted to higher frequencies compared to the position of the G-band of graphite ( $1581\text{ cm}^{-1}$ ) and is the result of the presence of certain double bonds which resonate at higher frequencies [6, 7]. After a complete reduction of graphene oxide to graphene this band usually shifts to the lower frequencies [4].

D-band of SLGO in LB film exhibits at  $1360\text{ cm}^{-1}$ , which characterizes the degree of imperfection of graphene and it is active only if the defects are involved in the double resonance scattering near the Brillouin zone [8]. Therefore commonly intensity ratio of  $I_D/I_G$  is used to establish the dimensions of the  $\text{sp}^2$ -domains in carbon materials. The obtained data indicate that the ratio of the intensities of G and D-bands was slightly increased with increasing of temperature. Typically, different authors show that this ratio should be reduced in the case of reduction of graphene oxide [5]. However, as shown in works of [9-14], the increase of  $I_D/I_G$  is associated with an increased formation of bonds defects or large number of small bonded  $\text{sp}^2$ -domains of carbon during the process of reduction. Also in disordered media, such as amorphous and crystalline graphite, increase of  $I_D/I_G$  ratio reveals the ordering process and increasing in the number of aromatic rings in the structure [15]. The possible presence of disordered regions in the structure of SLGO LB films indicates by the presence of 2D band in the Raman spectra. It is known that the position of this band and the ratio  $I_{2D}/I_G$ , are directly related to the number of layers of graphene nanostructures [15, 16]. As it is seen from the table, the annealing of the film at a temperature of  $200\text{ }^\circ\text{C}$  lead to a shift of 2D band toward lower frequencies. This means that during the heating process the thickness of the graphene oxide LB films of were decreased [16].

Thus, it can be concluded that the heat treatment leads to the partial reduction of disordered and high defective graphene oxide in the LB films, accompanied by ordering of amorphous  $\text{sp}^3$ -regions and their transition to the  $\text{sp}^2$ -bonded carbon clusters.

#### 4. Conclusion

The optical and structural properties of graphene oxide LB films at temperature influence were studied. It is shown that heating of the SLGO LB films over  $100\text{ }^\circ\text{C}$  leads to the decrease in the optical density of the samples. The film structure is not changed. As shown by measurements of Raman spectra, there is partial reduction of disordered and high defective graphene oxide in the LB films, accompanied by ordering of amorphous  $\text{sp}^3$ -regions and their transition to the  $\text{sp}^2$ -bonded carbon clusters as well as a decrease in the thickness of the LB films.

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