Effect of Subphase Conditions on the Formation of Graphene Langmuir layers

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Abstract. This paper presents a study of the formation of graphene layers by Langmuir-Blodgett (LB) technique. The effect of subphase pH and temperature on the graphene Langmuir isotherms are investigated. Also, the influence of subphase conditions on the surface potential of a monolayer was reported. A variation in the pH of the water subphase can lead to change in the electrostatic interactions that influence the compression of the layers. The mechanical characteristics of graphene layers variation under the influence of the subphase pH and temperature was investigated. Langmuir layers assembly is a useful method to manipulate the distribution of graphene layers at the air–water interface. Successful deposition of graphene layers at the air-water interface on a silicon substrate was performed by using Langmuir-Schaefer (LS) technique.

1. Introduction

Graphene sheet recently attracted attention thanks to its electrical properties (transparent conductor) which makes graphene sheets a good candidate for the formation of novel materials with a wide potential for applications such ones as used in photovoltaic devices [1][2]. The graphene sheets properties can be tuned by oxidation and conversion of the materials from hydrophobic to hydrophilic. The assembly of graphene sheets into thin films can be formed with different methods such as spray coating, dip coating and Langmuir Blodgett method. Langmuir Blodgett was used for study and formation of graphene thin film thanks to the advantage of this method that makes possible the formation of two dimensions of monolayer with control of limiting monolayer area and control of the thickness of thin film, etc [3]. The hydroxyl and epoxy functional groups attached to the hydrophobic graphene sheets and allow the formation of layers at an air-water interface [4]. The change of subphase parameters leads to the changes of the properties of the monolayer (such as thickness, interactions between layers and occupied area). There are several studies that used Langmuir Blodgett to produce films of graphene oxide and after that they can be thermally or chemically treated to form graphene [5][6].

The LB method allows the variation of graphene layers over large areas and control over the number of layers in the thin film. The control of thin film density by use of following the surface pressure of isotherm during layers compression of subphase temperature and acidity makes it possible to tune precisely the properties and structure of graphene film.
LS method for variation technique can provide interesting properties of graphene thin films on various solid substrates which can be suitable for a range of applications including optoelectronics and sensors.

2. Materials and methods
Graphene powder was purchased from Time-Nano Company (China) and dissolved in chloroform with low concentration of 0.0001g/ml. Graphene layers were investigated by using Langmuir-Blodgett trough (KSV Nima LB Trough Medium KN 1003, Finland) and Surface Potential Sensor (KSV NIMA, Finland) that has a sensitivity of ± 1mV. The temperature of subphase was controlled by using LOIP thermostat (Russia). The subphase of deionized water with resistance of about 18,2 MΩ×cm was used. Graphene solution, 600 µl was dropped on the surface of water. After 12 min period, symmetric movable barriers were compressed into a monolayer at the rate of 12 cm²/min. The changing in the surface pressure of layer was studied. Graphene thin film was transferred on the solid substrates by LS. The surface morphology of graphene sheets of thin film was investigated by scanning electron microscopy (SEM).

3. Results and discussion
The monolayer of graphene sheets was formed on the water surface at subphase temperature (19, 24, and 41°C) and studied by compression isotherms (Figure 1). With increasing subphase temperature of the occupied area of layer has been decreased from 68 cm² to 56 cm² at 19 and 41°C, respectively, and the maximum value of surface pressure is decreasing. This could be explained by the change of dissolution speed of a monolayer. The surface potential is decreasing with increase of subphase temperature. That means that the maximum concentration of graphene sheets on the water surface decreases and the maximum value of surface pressure decreases as well. The decrease of the subphase temperature causes an increase in the maximum occupied area, due to decreasing of a dissolution speed of molecules and increasing of their concentration at air-water interface. Figure 2 shows the SEM images of graphene sheets which are transferred on silicon substrate at surface pressure of 10 mN/m at the room temperature.

![Figure 1](image1.png)

**Figure 1.** Influence of subphase temperature on the Langmuir isotherm (a), and surface potential (b) of graphene layers.

Figure 3 shows the influence of subphase pH on the Langmuir isotherm of graphene layers. With the decrease of subphase pH (lower than 7) the occupied area and liquid expanded behavior become higher pronounced and the isotherms exhibit progressive increase of compressibility. The increasing of occupied area is attributed to the larger density of unionized graphene sheets at the air-water interface on a silicon substrate. As the hydrophillicity of graphene it can be tuned by the degree of
ionization of the carboxylic acid group through pH of water subphase [7]. In the case of subphase acidity, the graphene layers have larger amount of unionized carboxylic groups at the edges leading to hydrogen bonding between the sheets (high compact and non-overlapping of graphene sheets), and can be due to increasing of the hydrophobicity with increases of the acidity of subphase [8]. The surface potential value has been raised from 0.19 to 0.27 volt at low subphase pH (Figure 3b).

In contrast, the isotherm of graphene layer at subphase pH is higher than 7 and exhibits a slight increase in surface pressure. In the case of subphase pH 7 and higher, the layers are hydrophilic and the overlaps can happen due to the more ionized carboxylic groups and water serves as a lubrication layer cause overlapping graphene sheets slide over each other and lead to reduction of the occupied area of layers [3]. Another study showed that the increase in the hydrophilicity of the graphene sheets [9] at subphase pH 7 and higher may facilitate the overlapping and lead to decrease of the surface potential value.

Figure 2. SEM images of graphene layers on silicon substrate.

Figure 3. Influence of subphase pH on the Langmuir isotherm (a), and surface potential (b) of graphene layers.
The compressibility of the graphene layers (K) and the compression modulus (χ) for each condition were calculated, the results are presented in Table 1. These parameters were calculated by the following formulas:

\[ K = -\frac{1}{A_0} \left( \frac{dA}{d\pi} \right) \]

and

\[ \chi = \frac{1}{K} \]

**Table 1.** Characteristics of graphene layers at different subphase pH and temperature.

| pH | A cm² | K, m/mN | χ, mN/m | T °C | A cm² | K, m/mN | χ, mN/m |
|----|-------|---------|---------|------|-------|---------|---------|
| 7  | 66.56 | 0.0401  | 24.91   | 19   | 68.23 | 0.0404  | 24.74   |
| <7 | 93    | 0.0422  | 23.70   | 24   | 66.56 | 0.0401  | 24.91   |
| >7 | 71.38 | 0.0347  | 28.74   | 41   | 53.25 | 0.0359  | 27.80   |

Analysing the characteristics (K and χ) of the layers for various conditions, obviously, it can be noted that at the change of the subphase pH and temperature the mechanical properties of the layers change. The rigidity of the graphene layers increases at the lower subphase temperature, indicating increasing in the compressibility from 0.0359 to 0.0404 m/mN at 41 and 19 °C, respectively, with the compression modulus that correspondingly decreases. At the low subphase pH shown higher compressibility causes increase of the rigidity of layers (see Table 1).

4. Conclusion
We have studied the formation of graphene sheets at the air-water interface and the result showed that graphene layers are highly sensitive to subphase pH and temperature, which influences their hydrophilicity, dissolution speed, dispersibility and the interaction between graphene sheets. The mechanical characteristics of graphene layers change by the influence of subphase pH and temperature: the rigidity of the layers increases at the lower temperature and higher acidity. The understanding of these parameters can help us to form the required properties of graphene thin film for further applications.

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