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TOWARDS THE UNDERSTANDING OF THE MECHANISM OF DC PROTONIC CONDUCTION IN GRAPHENE OXIDE

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It is found the dependence of the graphene oxide dc electrical conduction vs. temperature at fixed air humidity levels (under the laboratory conditions) to be nonmonotonic with a pronounced maximum. The increasing of the conduction while the temperature drops corresponds to the protonic concentration increase due to water molecules adsorption as the result of condensation (chilled mirror effect). At this condensation process, the dew point temperature can be determined as the temperature of the fastest adsorption rate of water molecules (and the protonic conduction fastest increase vs. temperature). At some temperatures, either at 0 °C under atmospheric pressure, when the adsorbed water turns into ice, or at the dew point at $T < 0$ °C, at further temperature drop the protonic conductivity suddenly starts to exponentially decrease via the Arrhenius-type dependence with the activation energy of ≈ 0.7 eV.

Key words: graphene oxide; dc current; proton electrical conduction; water adsorption; dew point; activation energy; humidity sensor

INTRODUCTION

Graphene is a two-dimensional monolayer of sp^2-bonded carbon atoms exhibiting exceptional electrical properties [1, 2] and a great potential for ultrasensitive detection. Sensors based on graphene prepared via the micromechanical cleavage of graphite [3, 4] or via the reduction of graphene oxide (GO) [5–11] have raised significant interest. These sensors show very high sensitivity to gases, including NO_2, NH_3 and others. Sensors with single-molecule sensitivity have also been reported as well [12]. The mechanism of these ultrasensitive gas sensors is similar to that of carbon nanotube-based gas sensors [12–16].

Although some studies have reported water adsorption on graphene [17, 18], long time response and relatively low sensitivity eliminate applications [17]. Therefore, using this nanomaterial to fabricate humidity detection sensors remains difficult.

As an alternative material—the graphene precursor, GO, presents considerable advantage as a material for sensing applications, especially for water detection. Graphite oxide can be used to massively produce graphene and is water dispersible, thereby enabling subsequent exfoliation into few-layer nanostructures to form GO [15]. Thus producing continuous films from GO suspensions is fairly straightforward [16, 19–21].

The basal planes and edges of GO platelets are composed of distributed chemical groups containing oxygen [22–24], which can increase the hydrophilicity of GO and consequently enhance the sensitivity of the sensors to water [25]. In contrast to graphite with water intercalated molecules [26], GO more easily adsorbs water vapor from the gas phase.

Chemical groups make GO electronically insulating [27], which limits the graphene oxide use in the capacitive-type sensors, assuming capacitance mechanism of water adsorbed molecules only [28], or proton conductivity mechanism in GO [29, 30], initiated by water adsorbed molecules interacting with hydrophilic functional groups in GO, thus generating protons H^+ [31]. Besides, subsequent reduction of GO brings the electron (hole) conduction in the consideration, making the GO proton vs. electron conductivity tunable [32].

Instead, our goal is to stay with electronically insulating GO, and to study pure protonic transport in GO.

Our experimental approach is based on the direct current (DC) measurements vs. temperature at fixed and well-determined humidity levels, introducing specific values of protonic concentrations in GO films, assuming the statement of protonic conduction initiated by water adsorbed molecules [31] is valid.

MATERIALS AND METHODS

The graphene oxide film was prepared by using simple filtering method of the water solution (suspension) of graphene oxide nanoplateletes. The film was located close to Pt resistance temperature detector (RTD) on the surface of the temperature stage of the Cu "cold finger" in the vacuum sealed chamber with the intake and exhaust ports for the mixture of dry nitrogen flow from the liquid N_2 tank with moist N_2 from water bubbler, creating specific level of humidity in the chamber. The humidity level was controlled by the flow rate via flow meter and pressure controller and was measured precisely by a commercial dew-point meter. The bottom part of the Cu "cold finger" outside the chamber was immersed into the Dewar with liquid N_2 creating relatively slow (1–3 °C per minute) cooling of the stage down. The temperature dependence of the conductance G of the GO sample vs. temperature T was recorded at different fixed moisture levels.

RESULTS AND DISCUSSION

Surprisingly, the dependence of conductivity of GO film on temperature at fixed and relatively low humidity levels (for example, we consider the dew point set to $T_d = -24$ °C), possesses a beautiful peak-like behavior, as shown on the Fig. 1*a*). An attempt to analyze this type of the curves in the semi-log scale, as plotted on the Fig. 1*b*, shows the asymmetric shape. This means that we have a competition of totally different processes at the temperatures higher and lower T_d.

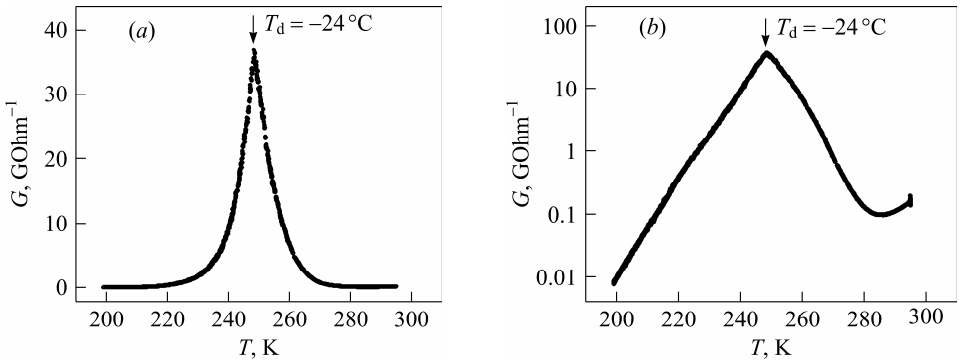

Figure 1. – (*a*) The typical dependence of electrical conduction *G* of GO film on temperature *T* at fixed and relatively low humidity levels ($T_d = -24$ °C) with a peak-like behavior. (*b*) The same curve in the semi-log scale

An attempt to build a plot of the left-hand side part of the dependence of the Fig. 1 in Arrhenius coordinates shows the straight line (Fig. 2).

The activation energy $E_a \approx 0.7$ eV calculated from this Arrhenius plot, described by the equation

$$G = G_0 \exp(-E_a/k_B T),$$

where G is the electrical conduction of GO film exposed to the water vapor, G_0 is the pre-exponential factor which weakly depends on temperature compared to the exponential, k_B is the Boltzmann constant and T is the absolute temperature.

The dependence of conductivity of GO film on temperature at much higher humidity levels (for example, the dew point set to $T_d = +12$ °C), shows the peak-like behavior as well with clearly observed saturation.

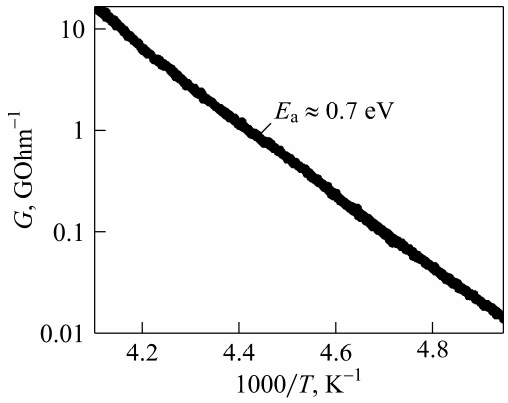

Figure 2. – The temperature dependence of the conductance of GO in Arrhenius coordinates (ln*G* vs. 1/*T*) with the activation energy $E_a \approx 0.7$ eV

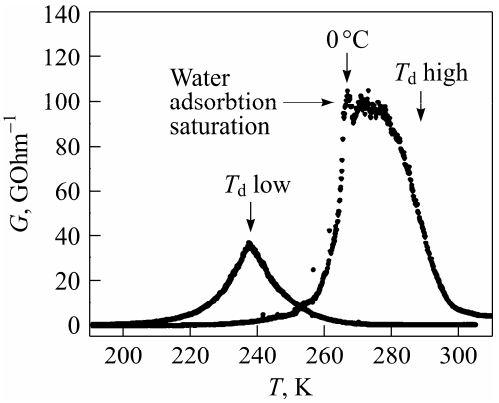

Figure 3. – The comparison of the dependence of conductivity of GO film on temperature at different fixed humidity levels (dew points set to $T_d = -24$ °C and $T_d = +12$ °C)

Our understanding of this temperature dependence of the conductance of GO with the maximum in the presence of humidity is the following. While the temperature drops, the water molecules adsorption on the surface of GO takes place as the result of condensation on the cold surface (chilled mirror effect). The interaction of water molecules with hydrophilic functional groups of GO generates protons H^+ [31].

It was accepted the protons to move by hopping between adjacent water molecules following Grotthuss mechanism [33]. However, protons believed to be hardly available in aqueous medium. In bulk water, most of the protons are attached to the H_2O molecules to form hydronium $(H_3O)^+$ cations [31]. Besides, our observation of protonic conductivity corresponds to the temperature range below water freezing. That is why, in our opinion, the protons likely to be hoping via proton-conducting sites on the surface of GO. The exact mechanism of proton conductivity in GO needs to be carefully examined.

CONCLUSIONS

The proton conduction in GO was found to be associated with the humidity level and the temperature variation.

The nonmonotonic behavior of the conductance of GO vs. temperature is based on the transition from water adsorption (protonic concentration increasing) to proton conduction mechanism with simple activation behavior. The activation energy of proton conduction was found to be close to 0.7 eV.

Graphene oxide films can be utilized as a new humidity sensor (hygrometer) platform with the direct determination of the dew point.

Our experimental results provide a new background for the analysis of the proton conduction mechanism in GO, based on water adsorption.

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ТЕОРЕТИЧЕСКОЕ ИССЛЕДОВАНИЕ ПОЛЕВЫХ ТРАНЗИСТОРОВ И РЕЗОНАНСНО-ТУННЕЛЬНЫХ ДИОДОВ НА ОСНОВЕ ГРАФЕНА

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В докладе описаны комбинированные модели полевых графеновых транзисторов (ПГТ) и резонансно-туннельных диодов (РТД) на основе графена. С их помощью исследованы вольт-амперные характеристики (ВАХ) приборов в различных режимах работы.

Ключевые слова: графен; комбинированные модели; полевой транзистор; моделирование; резонансно-туннельный диод; вольт-амперная характеристика.

THEORETICAL STUDIES OF FIELD-EFFECT TRANSISTORS AND RESONANT TUNNELING DIODES BASED ON GRAPHENE

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In the paper the combined models of graphene field-effect transistors and resonant tunneling diodes based on graphene are presented. IV-characteristics were investigated with the use of the proposed models in different operating mode.

Key words: graphene; combined models; field-effect transistor; simulation; resonant tunneling diode; IV-characteristic.