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# Unusual Optical Properties of Graphene on an Rh Surface

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Single- and multilayer graphene films formed on the surface of a number of metals (Rh, Pt, Ir, and Re) at the thermal decomposition of benzene molecules have been studied. A surprising phenomenon has been revealed: these films with thicknesses up to 15 layers do not absorb light emitted by the surface and affect neither brightness nor true temperatures of the surface, which contradicts the fundamental results obtained by A. Geim and K. Novoselov. At larger thicknesses, absorption occurs in agreement with the commonly accepted concepts.

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## INTRODUCTION

Surprising optical properties of graphene have been studied in detail in the last decade and A. Geim and K. Novoselov, who discovered these properties, were awarded with the Nobel Prize. As was shown in [1, 2], a multilayer graphene film absorbs visible light well and the degree of absorption of single-layer graphene is determined only by a combination of fundamental constants and is about 2.3% [3–6]. Since interlayer coupling is weak, it can be assumed that each of the layers in a multilayer film absorbs light independently; for this reason, the optical absorption coefficient of such a system can be calculated directly by Lambert's cosine law.

We and other groups have studied the formation of graphene and graphite on the surface of metals for the last four decades [7, 8]. We recently discovered and described a phase transition of a two-dimensional graphene film to three-dimensional graphite film on the surface of a carbonized metal (Rh) [9]. The detailed consideration of its kinetics, where a change in the brightness temperature of the surface plays a decisive role, stimulated detailed investigations of this problem because it seemed that the behavior of real systems on the surface of a metal is different from predictions based on the above concepts.

## EXPERIMENTS

The experiments were performed in high vacuum ($p \sim 10^{-10}$ Torr) with an Auger spectrometer with a resolution of $\Delta E/E \sim 0.1\%$ [10]. The samples under study were 40 × 0.02 × 1-mm metallic Rh ribbons, which were textured by direct ac heating and were cleaned from impurities by aging of heated ribbons in an oxygen atmosphere and in ultrahigh vacuum. After cleaning, the orientation of the surface of a ribbon in the (111) direction was 99.8%. The average size of grains was 40–50 μm. The surface was uniform in work function within an accuracy of 0.05 eV. In the chamber of the instrument, a unit was assembled for measuring the thermionic emission from heated samples. Auger spectra can be recorded directly from the samples heated up to 2000 K.

The samples were carbonized by the standard procedure of the aging of heated ribbons in the isothermal regime in a benzene atmosphere until carbon saturated the bulk of the sample to the extreme solubility and a graphene monolayer was formed on the surface of the sample. The carbonization procedure was discussed in detail in [11] for rhodium and in [8] for other metals (Re, Pt, Ni, Ir, etc.). Since a ribbon was thin, diffusion processes were fast and real thermodynamic equilibrium at temperatures above 1100–1200 K was reached in about several seconds. After that, benzene vapors were evacuated and a strictly monatomic graphene layer remained on the surface of the metal.

In the process of carbonization, carbon atoms penetrate into the bulk of the ribbon and can generally change its electric resistance and, thereby, the released power at a constant filament current. However, owing to a low extreme solubility of carbon atoms in Rh, this effect is beyond the measurement accuracy. In particular, in the carbonization temperature range of 1200–1800 K, a power increase owing to a change in the resistance was less than 0.5% and the brightness temperature of the ribbon remained constant with an accuracy that was ensured by an optical pyrometer (~4–5 K). The specific heat of the holders of the ribbon was chosen as low as possible. In this case, its middle part with a length of ~35 mm in the pyrometric

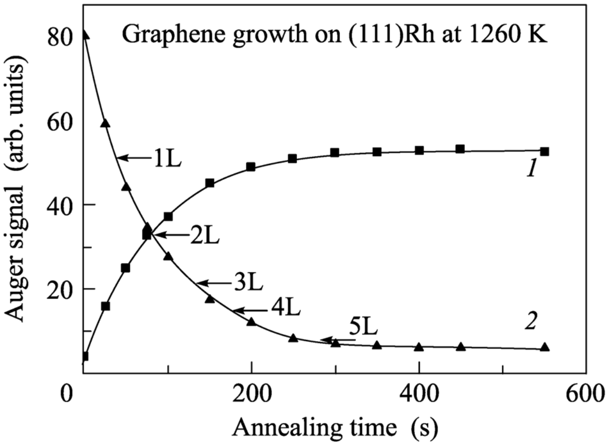

**Fig. 1.** Auger signals from (*1*) carbon and (*2*) Rh versus the heating time at 1260 K for the rhodium ribbon carbonized at $T_C = 1360$ K. Arrows mark the times of the formation of the respective graphene layer.

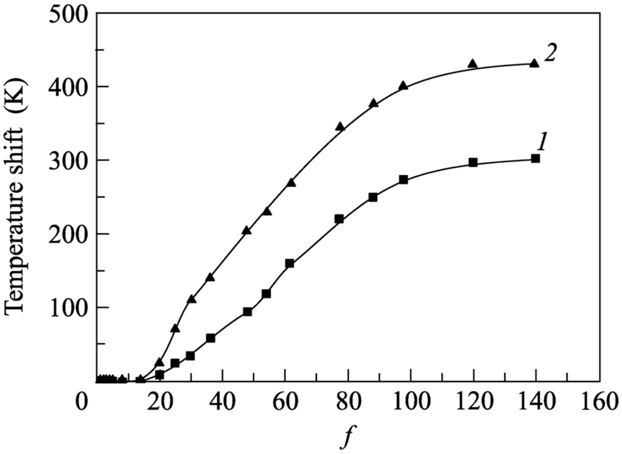

**Fig. 2.** (*1*) Brightness and (*2*) true temperature shifts of the graphene film grown on the Rh(111) surface versus the thickness of the film.

region was uniform in temperature with the same accuracy.

## GROWTH KINETICS OF GRAPHENE AND GRAPHITE LAYERS

If the temperature is abruptly reduced below the carbonization temperature $T_C$, the solid solution of carbon in a metal becomes supersaturated and excess carbon rises on the surface, forming graphene and graphite layers. The layer-by-layer growth of a graphite film was previously observed in metals Re [10], Pt [12], and Ni [13]. Both single- and multilayer films have the graphene (graphite) structure, which is confirmed by scanning tunnel microscopy and Raman scattering measurements.

The thickness (the number of layers $f$) in a graphene or graphite film formed on the surface at the reduction of the temperature is determined by the difference between the extreme solubilities of C in Rh at the carbonization temperature ($n_C(T_C)$) and at the film growth temperature ($n_C(T)$):

$$f = [n_C(T_C) - n_C(T)]N_{Rh}/2N_{CML}, \quad (1)$$

where $N_{Rh}$ is the number of rhodium atoms in the sample with the volume $V = Sh = 1\ \text{cm}^2 \times 2 \times 10^{-3}\ \text{cm} = 2 \times 10^{-3}\ \text{cm}^3$, $N_{CML} = 3.86 \times 10^{15}$ atoms/cm$^2$ is the concentration of carbon atoms in the graphene monolayer, and a coefficient of 1/2 is due to the separation of carbon simultaneously on both sides of the ribbon sample. The quantity $n_C(T)$ was presented in [14, 15] and was carefully measured in our work [16]. The calculations are in good agreement with the Auger spectroscopy data at the growth of a thin film ($f < 6$). (Auger spectroscopy is insensitive to thicker films.)

The variation kinetics of the Auger signals from the film ($E = 272$ eV) and substrate ($E = 302$ eV) at the release of carbon from the bulk onto the surface of rhodium carbonized at $T_C = 1340$ K and aged at $T = 1260$ K is shown in Fig. 1. The Auger signal of carbon increases and is saturated at the thickness of the film that is several times larger than the mean free path of Auger electrons with a given energy ($\lambda \sim 5$ Å) [17]. Simultaneously, the signal from the substrate is no longer detected because of its screening by carbon.

The calculation by Eq. (1) yields $f \sim 5$–6 layers. It is known that a graphene monolayer reduces the Auger signal from the substrate by a factor of 1.6 at the energy of electrons of 150–300 eV [17]. As can be seen in Fig. 1, the Auger signal from rhodium decreases by a factor of about 16, which corresponds to the indicated thickness of the film. At $T_C > 1400$ K and $T = 1260$ K, a film thicker than eight layers is formed and no Auger signal from the substrate is detected. The shape of the Auger signal from carbon is typical of graphite.

According to Fig. 1, the time of a decrease in the signal by a factor of 1.6 is almost the same throughout the entire curve. This indicates the layer-by-layer growth of the graphite film, as was previously observed for the Ni–C system [13]. The constant growth time of each layer shows that diffusion processes in the bulk are quite fast and growth is limited by the appearance of carbon atoms on the surface and nucleation of a new graphene layer [8].

## MEASUREMENT OF OPTICAL PROPERTIES

Figure 2 shows variation of the brightness and true temperatures of the sample at the growth of graphene and graphite. Because of the avalanche release of carbon at the reduction of the temperature, which was described in our work [9], these curves cannot be recorded in a direct experiment.

To record these curves, the experiment was performed as follows. The sample was successively carbonized with an increase in the temperature in the range of 1260–1800 K. After each carbonization cycle, benzene vapors were evacuated and the current flowing through the sample was abruptly reduced to a value corresponding to the formation of the film with the necessary thickness calculated by Eq. (1). (At a higher $T_C$ value, the grown film appeared to be thicker.) After reaching a steady state, the measured temperatures were plotted. We note that the electric power released in the sample after the growth of the film always coincided with the power scattered in the uncarbonized ribbon at the same heating current.

The brightness temperature was measured by a Piro color pyrometer at a wavelength of 580 nm. As can be seen in Fig. 2, it does not change at the growth of the graphite film with a thickness of up to 15 layers. At the time corresponding to 20 layers, it begins to decrease slightly. At 120 layers, this decrease corresponds to about 300 K. Then, the curve is stabilized and the temperature shift does not change with a further increase in the thickness of the film.

The variation of the true temperature was determined from a decrease in the thermal electron current at a constant electric power released in the bulk of the ribbon. (In the process of growth of the graphite film, this current decreases by five orders of magnitude!) We used the Richardson formula:

$$I^- = SAT^2\exp[-e\varphi/kT], \tag{2}$$

where $I^-$ is the current of thermal electrons, $S$ is the collection area, $A = 175$ A cm$^{-2}$ s$^{-1}$ is the Richardson constant for this surface, $k$ is the Boltzmann constant, and $e\varphi = 4.7$ eV is the work function of multilayer graphite, which we determined by the Richardson line method. The true temperature can be determined with a high accuracy if the collection area $S$ is constant and the work function is known.

To measure the work function for a thick film, we took $f > 100$, where the brightness temperature no longer depends on the thickness of the film. Assuming that the grayness value is $\varepsilon = 0.8$ [18], we calculated the true temperature from the formula [19]

$$1/T_{\mathrm{Br}} + 1/T = 4.62 \times 10^{-5}\ln(1/\varepsilon). \tag{3}$$

With the use of this temperature, the Richardson curve can be plotted for the multilayer film and the work function can be calculated with a high accuracy ($e\varphi$ = 4.7 eV).

Line *2* in Fig. 2 shows the true temperature shift in the sample with an increase in the thickness of the graphite film. Direct experimental data can be obtained only for $f < 30$ and $f > 120$. In the intermediate states, the current is too low. We note that the true temperature at the maximum thickness of the film decreases by $\Delta T \sim 430$ K, as was previously observed in [18].

We now describe how data are obtained. Let the carbonization temperature be $T_C = 1680$ K, $n_C$ = 0.19 at %, and a graphene monolayer exist on the surface. We abruptly reduce the heating current from 3.5 to 3.0 A, which would correspond to the temperature $T_1 = 1480$ K in the case of uncarbonized ribbon. Excess carbon from the bulk is segregated on the surface and forms the multilayer graphene film. This leads to an increase in the grayness value and radiative heat absorption and, thereby, to a decrease in the brightness and true temperatures, as well as in the thermal electron emission current. After the end of the process, we calculate the new true temperature by Eq. (2), $T_2 = 1380$ K, and determine the corresponding extreme solubility $n_C(1380\ \mathrm{K}) = 0.07$ at %. The number of layers in the graphene film can be easily estimated by Eq. (1) as $f = 33$. In this case, $\Delta T = T_1 - T_2 = 1480 - 1380 = 100$ K. In order to obtain a thicker film, the carbonization temperature should be higher.

Thus, neither the true nor brightness temperature changes for films thicker than 15 layers on the Rh substrate.

## GRAPHENE ON OTHER SUBSTRATES

In view of the results obtained, it was necessary to test how graphene films behave on other metallic substrates. Graphene on Ir(111), Pt(111), and Re(10-10) was grown as on rhodium by the chemical vapor deposition (CVD) of benzene molecules. The maximum number of layers on iridium was $f = 1$ and on platinum was $f = 10$ because of a low solubility. Multilayer films can be formed on rhenium, but diffusion processes in this case are much slower than those in the case of rhodium [8, 10].

Neither the brightness nor true temperature changes for films with thicknesses $f < 15$ on all substrates under study at a constant electric power released in the samples.

## DISCUSSION OF THE RESULTS

We now discuss the results. In the high-temperature region under consideration, heat loss on holders can be neglected owing to the temperature uniformity of the central part of a sample. Consequently, the electric power released in the ribbon is completely emitted from the surface; therefore,

$$IU = \varepsilon\sigma T^4, \tag{4}$$

where $I$ and $U$ are the current flowing through the ribbon and the voltage drop on it, respectively; $\varepsilon$ is the grayness value in the region of maximum radiation (~580 nm); $\sigma$ is the Stefan–Boltzmann constant; and $T$ is the true temperature. The left-hand side of Eq. (4) (released power) was maintained constant in the experiment. As graphite grew, the emissivity varied from ε = 0.24 [19], which corresponds to a pure metal, to ε = 0.8 [19], which corresponds to graphite. The brightness temperature $T_{\mathrm{Br}}$, which is related to the true temperature $T$ by Eq. (3), varied simultaneously.

It seems surprising that the appearance of graphene and graphite on the surface at the initial stage of their growth affects neither brightness nor true temperature. Within the simplest equilibrium model, it would be expected that graphene layers forming on the surface, which have the same temperature as the substrate, absorb light emitted by the metal with the coefficient ε = 0.2–0.3 and reemit it with ε = 0.8. This model satisfactorily describes effects in thick films. However, it is inapplicable to thin films when both brightness and true temperatures remain unchanged.

This is possible under the assumption that graphene on the metal surface does not absorb light for a certain reason and the multilayer film remains optically transparent up to a certain thickness; after that, it begins to absorb and emit light. This phenomenon is apparently quite general. It is probably due to a change in the electronic properties of graphene because of the interaction with the metallic substrate. At present, we cannot propose any model to describe the observed phenomenon.

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