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## MODIFIED GRAPHENE-LIKE FILMS AS A NEW CLASS OF SEMICONDUCTORS WITH A VARIABLE ENERGY GAP

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It has been theoretically predicted and experimentally proved that the deformation of thin graphite-like carbon films is accompanied by the appearance of an energy gap at the  $K$ -point, the gap being proportional to a strain. A metal-semiconductor phase transition in a thin graphite (or multilayered graphene) film has been revealed. This phenomenon can be promising for the development of semiconducting materials.

### 1. Introduction

Crystalline carbon exists in two allotropic forms, namely,  $sp^3$  (diamond, an insulator with an extremely hard crystal lattice) and  $sp^2$  ones (graphite, a fragile semimetal). Mixed  $sp^2/sp^3$  forms have also been intensively studied for recent years. These include (i) amorphous carbon (see work [1]), where there is no long-range crystalline order, but there are localized  $p$ -electrons, and which is described by the Anderson model [2], and (ii) diamond-like carbon films that contain a considerable amount of hybridized  $sp^3$  atoms of carbon, but can include a significant amount of hydrogen atoms as well. Depending on the fabrication conditions, such films can either be completely amorphous or contain diamond crystallites [3].

An additional impetus to those researches was given by the intense development of the physics of graphene (see, e.g., reviews [5, 6]). The creation of a graphene-based field transistor is known to meet basic difficulties. The absence of the energy gap in graphene results in that it is difficult to obtain substantial resistance changes required to create two states – conducting and not conducting, on which the binary logic is based – by applying any voltage to the gate. Hence, it is necessary to form such an energy gap in graphene that thermally excited charge carriers would give a small contribution to conductivity at operating temperatures.

A probable way to do this consists in the fabrication of graphene nano-ribbons, where quantum dimensional effects allow one to obtain an energy gap with a necessary width (a ribbon width of 20 nm corresponds to an energy

gap equivalent to room temperature in terms of energy units) [6]. Another probable approach consists in the hydrogenation of the graphene surface and the formation of the so-called graphane, in which the energy gap does exist [7]. There also exist other approaches associated with the replacement of hydrogen by fluorine, introducing mechanical stresses and defects into graphene, and so on (see work [5]). However, it is premature to speak about the final solution to this problem.

From this point of view, of large interest can be the study of thin (of a few monolayers) carbon films. The presence of Dirac fermions in superthin graphite is testified by the results of researches using angle-resolved photoemission spectroscopy [8], scanning tunnel spectroscopy [9], and infra-red reflection [10] methods. The presence of such fermions is evidenced by experiments on the unconventional integer quantum Hall effect (IQHE) in thin graphite that had been observed for the first time even before monoatomic graphene was obtained [11], though a theoretical relation between the IQHE phenomenon and the Dirac spectrum of charge carriers was established somewhat later on [12], already on the basis of experiments dealing with monoatomic graphene.

At the same time, the properties of amorphous carbon hydrogenated with hydrogen (a-C:H films) strongly depend on the hydrogen concentration and state [3]. Actually, those films are new two-component compounds with a hydrogen ( $H_2$ ) content of about 50%, in which the short-range order looks like a distorted tetrahedral diamond-like structure  $sp^3$ . On the other hand, they contain hexagonal components  $sp^2$ , and the ratio between those two structures can change within a wide range, depending on the fabrication technique, temperature, thickness, and so on. To obtain specific data concerning the “coexistence” between those two absolutely different structures, we studied their optical spectral dependences, which are governed by the electron structure of the substance. The magnitude of the ratio  $sp^3/sp^2$  turned out to depend strongly on the number and the kind of structural defects.

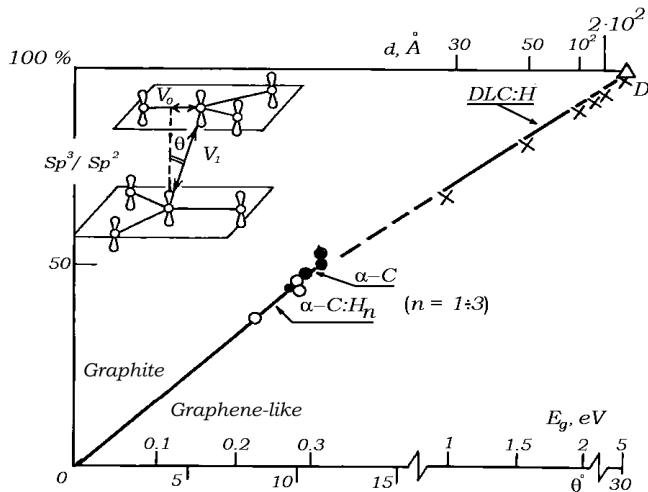


Fig. 1. Dependence of deformation-induced energy gap width  $E_g$  on the angle  $\theta$  and the ratio  $sp^3/sp^2$  for various carbon modifications ( $d$  is the size of  $sp^3$  cluster, see work [19])

Previous publications by the authors [13–18], the results of which were summarized in review [19], showed that the metallic properties of defect films transform into  $d$ -semiconducting ones. The theoretical analysis of ribbon structures with damaged chemical groups  $sp^2$ , which was carried out in the linear combination of atomic orbitals approximation, also testifies to the appearance of an energy gap, the width of which is proportional to the lattice distortion degree. **It is of importance that the effect takes place not only in amorphous carbon, where it has been studied by other authors as well [1], but also in thin (down to 0.5  $\mu\text{m}$ ) films of single-crystalline graphite.**

The qualitative mechanism of this phenomenon can be related to the emergence of effective partial  $sp^3$  bonds and be described as a variation of the displacement angle of one monolayer in perfect graphite with respect to the other one (i.e., as a shift of one layer with respect to the other). We assert that the presence of certain point defects can be used in a useful engineering approach for the creation of a new class of carbon semiconductors that can be implemented in micro- and nano-electronics (in particular, for the creation of field transistors as well).

## 2. Theoretical Models

As was shown in work [15], a forbidden gap arises at the  $K$ -point of deformed thin graphite (the deformation measure is an angle  $\theta$  (see the inset in Fig. 1); the non-deformed case corresponds to  $\theta = 0$ ). The gap magni-

tude equals

$$E_g = \frac{V_0^2 \sin^2 \theta}{2V_1 + \Delta}, \quad (1)$$

where

$$\Delta = 2V_1(\cos \theta \cos(\pi \cos \theta + kd \sin \theta) - 1) +$$

$$+ 2V_0 \frac{d^2}{a^2} \sin \theta (\pi \sin \theta + kd \cos \theta),$$

$k^2 = k_x^2 + k_y^2$ , the graphene lattice constant  $a = 0.246$  nm, the distance between graphene planes in thin graphite  $d = 0.4$  nm, and  $V_0 = 2.39$  eV and  $V_1 = 0.4$  eV are the matrix elements of interatomic  $\sigma$ - and  $\pi$ -bonds, respectively.

As was demonstrated in work [19], the angle  $\theta$  in thin graphite (or, according to modern terminology, in *multilayered graphene*) is proportional – in the small deformation approximation – to the ratio between  $N_D$ , the number of  $sp^3$  bonds, which insert perturbations into multilayered graphene, and  $N_0$ , the number of  $sp^2$  bonds. The substitution of carbon parameters to Eq. (1) results in a  $\theta$ -value of about  $10^\circ$  and an energy gap of about 0.3 eV.

An illustration of how the band structure in hexagonal graphite-like thin carbon transforms at that is presented in Fig. 2.

It is important to emphasize that the linear dispersion law  $E = \pm v k$  takes place at the  $K$ -point of a non-deformed graphene layer (see also works [5, 6]), whereas the ordinary parabolic dispersion of the band spectrum,  $E = E_0 \pm \frac{\hbar^2 k^2}{2m^*}$ , is realized for typical semiconductors, as well as at other special points ( $\Gamma, M$ ). Such a band spectrum of graphene results in an abnormally high mobility of its charge carriers (the corresponding theoretical upper limit amounts to about  $10^6$  cm $^2$ /(V · s), providing the carrier scattering at characteristic acoustic phonons), which could be very promising for future superhigh-frequency electronics in the case if graphene could be provided with characteristics of a semiconductor, but not lowering the mobility of its charge carriers.

At the same time, as was shown in the framework of the randomly ordered cluster model [1], a similar gap arises in amorphous carbon,

$$E_g = 2\beta M^{-0.5}. \quad (2)$$

Here,  $\beta = 2.9$  eV, and  $M$  is the number of benzene-like rings in the cluster. Note that the approach used in work [1] is opposite to that used in our work [14]; namely, a

completely disordered structure was a starting point in the former case, and a nonperturbed ordered structure of thin graphite (multilayered graphene) in the latter one.

### 3. Experimental Part

We can obtain diamond-like carbon films that have, on the average, an amorphous structure with distorted elementary cells, by using the technique of chemical deposition from the vapor ( $T = 200 - 300$  °C, the combustible mixture  $\text{CH}_4\text{-H}_2$ , the pressure in a chamber is 0.1–0.8 Torr,  $V \approx 2000$  V), and a Si substrate as a cathode. A radio-frequency (13.5 MHz) generator was used for the plasma generation. The film thickness changed within the range of 0.1–1  $\mu\text{m}$ . The film microhardness was about 2 GPa, but, after the implantation of  $\text{N}^+$  ions, it grew to 8 GPa [18]. The analysis of an external morphology carried out with the use of the electron or atomic force microscope revealed a porous or globule-like structure.

A different method was used at the fabrication of graphite-like carbon films. The latter were obtained by depositing low-energy (1–2 eV) carbon atoms from a gas plasma onto a copper substrate in vacuum and at room temperature. Hydrogen ( $\text{H}_2$ ) was added into the gas mixture, and no additional annealing was carried out. The so-fabricated films had a low density ( $\rho = 2.4 - 2.5 \text{ g/cm}^2$ ), a high microhardness  $H \approx 35$  GPa, a resistance of  $10^4 - 10^5 \Omega \cdot \text{cm}$ , and a thickness of 0.5–10  $\mu\text{m}$ .

The optical energy gap was determined by analyzing the spectral ellipsometry data making use of the Tauc equation (the dependence  $[\alpha(h\nu)]^{1/2}$  versus  $h\nu$  was extrapolated by a straight line). In so doing, the tails in the long-wave range were used to determine the line half-width  $H$ , which is known as a “measure of distortion”:  $H \sim N_D$ . More exact values were obtained by analyzing the area of the “tails”.

The spectral dependences of optical constants in the IR range were calculated, by using the reflection spectra. The optical parameters were found, by taking two surfaces of reflection into account. Calculations were carried out with the use of an optimization procedure (see work [17]). In such a manner, by examining the form of long-wave “tails”, it was possible to draw conclusion concerning the measure of film deficiency. As was indicated in earlier works [15, 16, 19], three peculiarities can be observed in the absorption spectra for practically each specimen. Two peculiarities – at about  $\lambda = 3$  and 7  $\mu\text{m}$  – correspond to C–H<sub>n</sub> ( $n = 1 - 3$ ) and C–C carbon bonds, respectively. The third peculiarity (at  $\lambda = 4.5 \mu\text{m}$ ) is as-

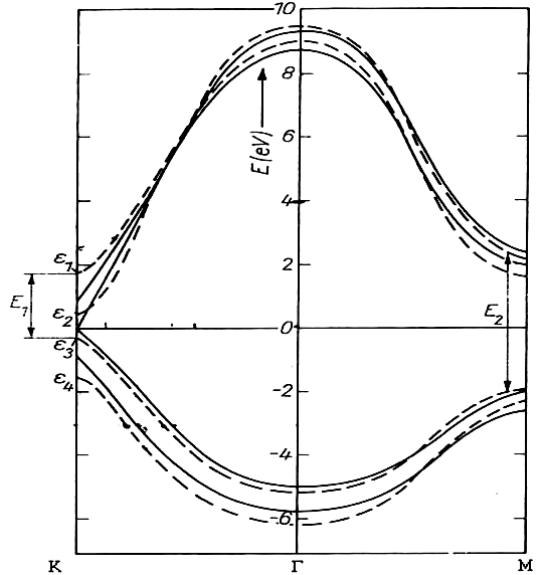


Fig. 2. Band structure in thin graphite-like carbon (solid curves) and in carbon with induced deformations, and an energy gap induced by deformations at the  $K$ -point (dashed curves) [14, 15]

sociated with a transition through the forbidden gap  $E_g$ ; it appears owing to the split described above at the point  $k = 0$ , which is caused by the elementary cell deformation (induced by defects, mechanical squeezing, and so on).

To vary the type and the number of defects, we used, besides the modification of technological regimes, the procedure of ion implantation with  $\text{N}^+$ ,  $\text{Ar}^+$ ,  $\text{C}^+$ , and  $\text{H}^+$  ions. The dependence of the deformation-induced energy gap width  $E_g$  on the angle  $\theta$  for various carbon modifications is exhibited in Fig. 1.

The dependences of the energy gap magnitudes  $E_{g1}$  and  $E_{g2}$  (see Fig. 2) on the deficiency degree in superthin films, which were calculated from a broadening of the optical line half-width  $H$ , are depicted in Fig. 3.

### 4. Conclusions

Our experimental results are in good agreement with theoretical predictions (Eq. (1)). The estimates obtained for deformations invoked in graphite-like films and resulting in the corresponding splittings fall within a reasonable interval of low strains. At the same time, for higher deformations, the theory describes well the results obtained for amorphous carbon. We note that the description of those results by relation (2) meets substantial difficulties [1].

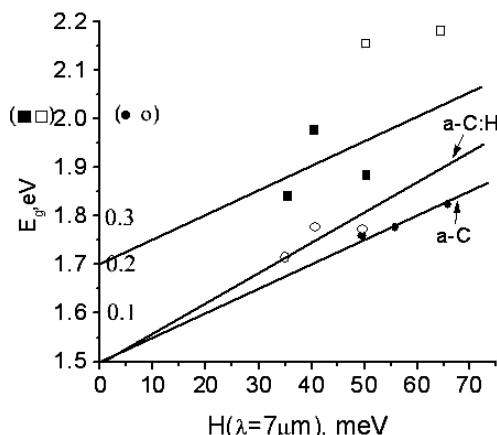


Fig. 3. Dependences of energy gaps in thin graphene films on the line broadening (the deficiency degree). The upper line corresponds to  $E_{g1} = \varepsilon_1 - \varepsilon_3$ , the lower ones to  $E_{g2} = \varepsilon_2 - \varepsilon_3$  (see Fig. 1).

Hence, we may assert that a thin semimetallic graphite layer transforms into a semiconductor already at low elastic strains, when structural defects are introduced, or at the doping. The physical nature of such phase transition has been determined: it is related to the bond distortion owing to the mixed hybridization  $sp^2 - sp^3$ , the phenomenon being possible only for carbon capable of the polyhybrid bonding. The discovered metal–semiconductor phase transition in a thin graphite (or multilayered graphene) film is promising for the materials science of semiconductors.

It should be marked that it is multilayered graphene (thin graphite) grown up, e.g., on the basis of SiC that is regarded today more and more often as a promising substance for technological applications, in contrast to monoatomic graphene. This fact is associated with a considerably higher quality of individual graphene planes in the bulk of thin graphite – and, as a consequence, with a very high mobility of charge carriers (up to  $10^6 \text{ cm}^2/(\text{V} \cdot \text{s})$ ) – in comparison with the worse structure quality of monoatomic graphene on a substrate – and, as a consequence, with the corresponding mobility of charge carriers that is one to two orders of magnitude lower [11].

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МОДИФІКОВАНІ ГРАФЕНОПОДІБНІ ПЛІВКИ ЯК НОВИЙ КЛАС НАПІВПРОВІДНИКІВ ЗІ ЗМІННОЮ ШИРИНОЮ ЗАБОРОНЕНОЇ ЗОНИ

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Р е з ю м е

Теоретично передбачено й експериментально доведено, що в деформованих плівках тонкого графітоподібного вуглецю в К-точці з'являється заборонена зона, пропорційна до міри дефектності плівки. Виявлений фазовий перехід метал–напівпровідник у тонкій графітовій (або багатошаровій графеновій) плівці може виявитися перспективним в інженерії напівпровідникових матеріалів.