Identification of Turbostratic Bilayer Grephene in Carbon Tribolayers

A. Mailian[1, 2, *], Zh. Panosyan[2], Y. Yengibaryan[2], N. Margaryan[2], M. Mailian[3]

[1]Center for Scientific Information, Institute for Informatics, Yerevan, Armenia

[2]Heliotechnic Laboratory, State Engineering University, Yerevan, Armenia

[3]DCV Group, LTX–Credence, Yerevan, Armenia

Email address:

amailian@ipia.sci.am (A. Mailian)

[*]Corresponding author

Abstract: It is expected that friction forces should cause drastic changes in the structure of rubbed off trace of sp^2 bulk graphite (carbon tribolayer or CTL). In this work we studied some properties of CTL. It is found that CTL contains segments of different transmission of light unique to carbon allotropes different from sp^2. X-ray diffraction (XRD) pattern, optical absorption spectra reveal a sp^2 crystalline structure on the surface of CTL. The Raman spectrum shows distinguished and narrow peaks with symmetrical line shape. Intensity ratio of 2D and G peaks is close to 1 which is characteristic of two-layer graphene. Increased interlayers pacing measured by XRD as well as symmetry of 2D peak of Raman spectra testifies to the presence of turbostratic two-layer sp^2 phase at the surface of CTL.

Keywords: Tribology, Raman Spectra, Turbostratic Graphene

1. Introduction

The straight forward method applied in pioneering work of obtaining of single-layer carbon [1] triggered another tendency of searching of simple methods of grapheme fabrication besides complex technological solutions. Among them, tribologically obtained carbon layer on a substrate at tracted researchers' attention mainly for its extreme simplicity [2 – 4]. It was found that such layers exhibit properties of sliced solid state material as well as properties of nanoscale thick carbon structures [5]. Some attempts were made to use them in sensors [6 – 8].

Though some initial investigations revealed them to be promising for using inflexible electronics, there is a room for investigation of physical and chemical properties of CTL. In addition, rubbing a layer under a single factor of pressure is likely to trigger a process of self-organization and hence the growth of CTL is probable to be rather complicated as well as multistep procedure.
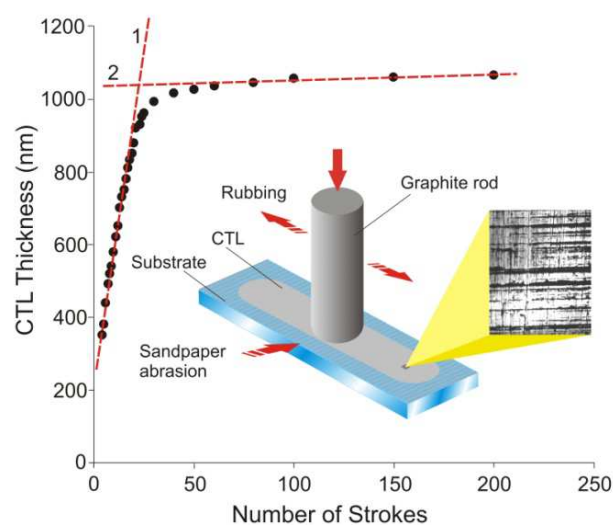
2. Experimental

Figure 1. Wear characteristics and obtaining scheme of CTL (inset). Magnified the through-thickness optical image of a segment of CTL is shown.

Due to its structural anisotropy carbon is a relevant material for peeling nanoscale thick layers. CTLs investigated in present work were obtained by repetitive rubbing a commercially available graphite bulk against insulating and transparent NaCl substrate (Figure 1, inset). The surface roughness of substrates was controlled by processing with sandpaper of different grain size. Obtained rough surface contained straight and parallel scratches dug by abrasive grains of sandpaper. Then, the graphite layer was obtained by stroke-by-stroke rubbing a rod of graphite along the same path (at 90° to the substrate surface) against the processed surface. Constant pressure of about 5 MPa was applied on the rod during the whole rubbing cycle.

Optical microscopy observation revealed a specific pattern of developed CTL. Vast areas of CTL become visually transparent and remain such even after multiple strokes. The thickness of the CTL was estimated based on assumption that the worn part of graphite rod is fully transferred and pressed onto the surface of substrate [9].

3. Results and Discussion

The distinguishing feature of rubbing is that friction stipulates the morphology, physical and chemical properties of tribolayers [10]. The initial layer is formed by the first stroke of parent graphite bulk on the surface of bare substrate. Then, with each stroke, the carbon layer evolves and the friction occurs between the surface layer of the graphite bulk and the surface of the CTL modified during the previous stroke. This sequence of layers development suggests that during rubbing peculiar physical processes should take place at perpetual changing interface between the friction surfaces of rubbed layer and bulk graphite. From tribological point of view, during rubbing the layers are formed and modified by a combined mechanical action of sliding and cleaving the basic carbon layers close to surface of graphite bulk, and consequent combined transfer and squash the graphite flakes onto the substrate surface. As it was reported previously, the evolution of CTL goes through two different stages [9]. In the first stage (marked as 1 in Figure 1) the wear rate, i.e. wear per stroke, is high. Then at a certain period of strokes number (~ 25 to 40 for the sample shown in Figure 1) the second stage runs in (marked as 2 in Figure 1). It exposes much lower wear rate and coefficient of friction. This behavior testifies to abrupt structural transmission occurring in CTL in the turning period. Since only one factor is responsible for CTL formation, the pressure, it is quite reasonable to suggest that final form of CTL is a result of self-organization [10].

We traced the changes in evolving CTL by measuring optical absorption (Figure 2). The spectra of optical absorption change qualitatively with each step. The fingerprint of nanoscale thick sp^2 carbon with a peak at 4.6 eV becomes evident after multiple strokes (about 4 for the sample shown in Figure 2). Then, the peak progressively dominates the spectrum as the number of strokes grows.
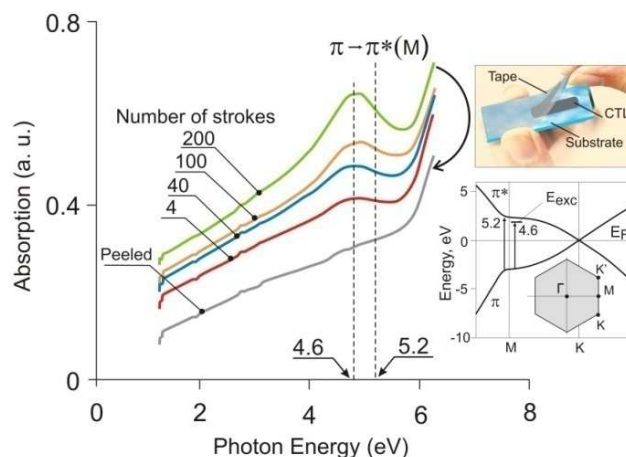

Figure 2. Variation of optical absorption spectrum with sequential rubbing and peeling. Inset shows band diagram and Brillouin zones of carbon hexagonal structure. E_{exc} is the energy of excitonic optical transition.

In order to study the role of surface layers in optical response of CTL, we followed the transformation of absorption spectrum by peeling the sample surface with Scotch tape (Figure 2). With peeling, the optical absorption at 4.6 eV decayed and the absorption at higher energy dominated the whole absorption (Figure 2). That spectrum closely resembled the optical response of mostly sp^3 bonded amorphous or diamond-like carbon (DLC) [11].

XRD study of as-obtained CTL found a crystalline structure on the sample surface (Figure 1). The XRD pattern exposed a (002) diffraction line at $2\theta = 26.551°$ emerging over a broad and noisy background. Note that no additional feature is observed. Such a XRD pattern is characteristic of a sandwich-like structure containing two basic layers of sp^2 carbon [12]. The peak disappears after peeling the surface with Scotch tape. This result tells about the existence of a thicker non-ordered phase beneath the sp^2 crystalline structure of surface.
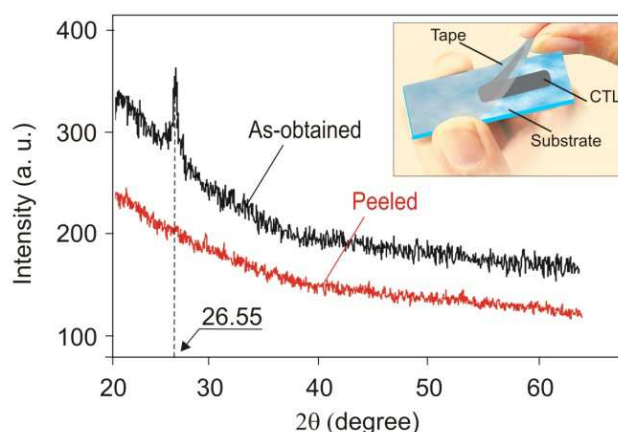

Figure 3. XRD pattern of CTL. The spectra were obtained for as-obtained and peeled surface samples. For peeling, conventional Scotch tape was used.

From these observations, it became apparent that CTL contains both sp^2 and sp^3 phases. Consequently, the optical absorption through the thickness of transparent areas should be the resultant of absorption in both sp^2 and sp^3 phases.

Absorption signal can be the sum of signals when the structures of both phases are arranged in either of two configurations: 1) transparent and separate sp^2 and sp^3 isles or 2) sandwich-like structure of sp^2 and sp^3 layers. Note that, sp^2 carbon is opaque for visible light with absorption of 2.3% per monolayer [13]. In addition, any structural deviation from sp^2 makes the crystal transparent. In transparent section of as-obtained CTL we found no area of CTL thinner than 10 nm (about 30 monolayers). The layer of that thickness and if it contains only sp^2 phase should absorb more than 60% of incident light. This means that no transparent isle of sp^2 carbon can be in CTL, i.e. the islet model should be excluded. Hence, signal overlapping can occur when the sp^2 structure is thin enough to transmit the light while the thicker transparent structure should be of a derivative from sp^2. This explains XRD results.

Raman spectroscopy confirms the suggested CTL structure (Figure 4). Note that, the peeled CTL did not exhibit any Raman feature worth for consideration. Some special CTL features in Raman reflect the CTL structure and morphology. First, typical Raman spectrum of CTL has all main features for hexagonal carbon lattice. The narrow peaks testify to discrete bond lengths and strong periodicity of crystal structure. On the other hand the dominant intensity of D peak is from highly defected structure. Next, the peaks are symmetrical which is different from Raman line shape of crystalline carbon.
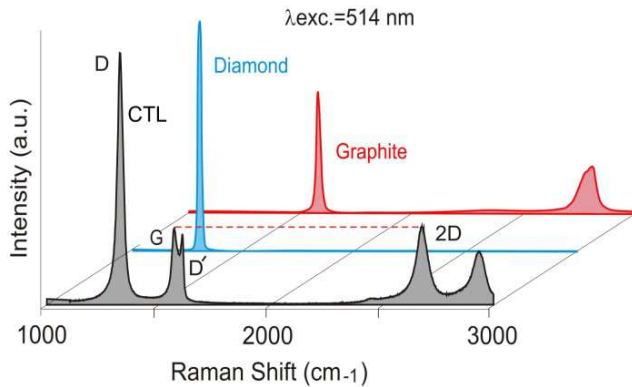

Figure 4. *Typical Raman spectrum for CTL (black line). For comparison Raman spectra of diamond and crystalline graphite are given too*

The thickness of carbon structure contributing in Raman scattering is easily determined from the relative intensity and shape of 2D peak which is more sensitive peak to stacking sequence [14]. The peak symmetry of 2D peak around resonance frequency has to be interpreted more detailed. The matter is 2D peak in Raman spectrum can be symmetrical for two types of sp^2 carbon: 1) single-layer and 2) displaced two-layer. In the latter case the full width at half maximum (FHWM) of the peak should be twice large.

Now, in case of CTL intensity ratio of 2D and G peaks $I_{2D}/I_G \sim 1$ which unmistakably shows that the upmost structure consists of two basic planes. In addition, FHWM is twice ($\sim$ 65 cm^{-1}) of the same characteristics of single layer. Since Bernal stacking bilayer grapheme should not exhibit peak symmetry it is natural to assume that the two upmost layers

of CTL are not arranged in Bernal stacking. This assumption is proved also with data obtained from XRD measurements that spacing between topmost monolayers is 0.3362 nm which is larger than in Bernal stacked crystalline graphite. This value is close to characteristic spacing for turbostratic bilayer grapheme [15]. This means that friction forces have displaced two topmost sp^2 single layers relatively each to other and 2D peak for these layers should be symmetrical as in case of CTL.

Upon further analysis we compare Raman spectrum of CTL with spectra of two most stable carbon morphological structures with the same type of chemical bonds – graphite and diamond. Since the bond length is the shortest, hence the bond strength is the highest in hexagonal stacked graphite, it is the most hard and stable structure in in-plane direction. In Raman mode the vibration of pure sp^2 bonds causes G and 2D peaks at $\sim$ 1580 and 2700 cm^{-1} respectively. G peak characterizes the in-plane vibration of hexagonal rings and is the fingerprint of honeycomb crystal structure. Any deviation from that configuration which compulsory gives rise to a peak in Raman spectrum at frequency of about $\sim$ 1340 cm^{-1} can be considered as defective. The further most deviation from sp^2 morphology is pure sp^3 bonded diamond which exhibits no other than D peak at 1333 cm^{-1}.

Comparing the peak location (ω) on Raman spectra of diamond and graphite bonds responsible for the peaks we found that the following rule is true [16]: $\omega r^2 = const$ where, r is the bond length.

The same relation for stretching vibration frequency of diatom bonds has been disclosed in early studies of covalent bonds [17, 18]. Later the rule was elucidated using a free-electron interpretation for a series of diatomic molecules [19]. For C–C bond the value of constant is found to be $2.8 \cdot 10^{-13}$ cm over all electronic states. For the Raman spectrum, shown in Figure 4, we obtained $3.2 \cdot 10^{-13}$ cm for both G and D bands. As for practical use of that relation, the frequency axis in Raman spectrum should be rescaled to bond length to interpret the features of Raman spectra.

4. Conclusion

Friction forces cause phase transformation in CTL. The topmost stratum of CTL is turbostratic bilayer grapheme and underneath part of the entire CTL is a deviation from sp^2 carbon. Both structures contribute in optical and vibrational characteristics of the whole CTL and reflect the features of covalent bonds. In particular, the lengths of bonds responsible for physical properties of CTL can be estimated applying spectral-structural relation $\omega r^2 = const$.

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