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Features of Raman light scattering spectra in the 2100 cm^{-1} line region by carbon formations in thin gradient gold films

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Raman scattering spectra of linear carbon chains (carbines) localized in thin gold films of variable thickness are investigated. It is shown that the integral line is inhomogeneous, and separate components are identified, the intensity of which depends in a non-trivial way on the thickness of the film. Qualitative explanations of the detected effects are proposed.

Keywords: carbine, linear allotropy of carbon, localization on clusters.

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1. Introduction

Carbon is one of the most widespread chemical elements on the Earth. It exists in different forms both on the Earth and in space. It is the basis of all known forms of life in the plant and animal world, as well as in the microorganism world. In the inorganic world carbon is included in different compounds and exists in a number of its own allotropes. Well known are three-dimensional and two-dimensional forms of carbon, diamond and graphite, which are built by carbon in sp^3- and sp^2-configurations of atomic orbitals [1]. It is worth to note that the most explicit form of coordinated sp^2-carbon is graphene [2]. Carbon tubes [3] and even fullerenes [4] can be considered as derivatives of graphene. It is less known that carbon can form one-dimensional carbon chains made up of carbon atoms with sp-hybridization of orbitals.

Meanwhile, the issue of one-dimensional carbon chains has a long history. First attempts to produce one-dimensional chains of carbon date back to the XIX century [5]. A one-dimensional carbon chain can be built in two ways: as a sequence of atoms bound by double bonds $=\mathrm{C}=\mathrm{C}=$ (cumulene) or as a sequence bound by alternating univalent and trivalent bonds $\equiv\mathrm{C}-\mathrm{C}\equiv\mathrm{C}-\mathrm{C}\equiv$ (polyyne). In literature such structures have received the name of linear carbon chains (LCC). If a polyyne LCC is terminated with hydrogen atoms, then this particle is named polyyne as well. A significant progress in research in this field has been made after the works of Kudryavtsev et al. [6,7], which allowed formulating more detailed issues. In particular, significant were the issues regarding the length of chains and the possibility to form macroscopic material from one-dimensional chains. It is customary to name such material as carbyne. Signs of natural formation of macroscopic amounts of carbyne have been observed in such media as graphite after shock loads, interstellar dust and meteorites. Also, it has been probably found in some laboratory experiments [8,9]. Nevertheless, in publications the use of „carbyne" term can be found regarding carbon chains without details of their lengths.

It was found quite early that carbon chains must have a specific feature in Raman scattering spectra. The triple covalent bond $-\mathrm{C}\equiv\mathrm{C}-$ between carbon atoms should be characterized by a typical line near 2100 cm^{-1} [10]. In modern studies this line is denoted as C-mode. Note that in [11] it is noted that the low-energy part of C-line (1980 cm^{-1}) is connected with the scattering on cumulenes. Also, it has been found that exact position of the line may vary depending on the number of links and on fragments attached to the terminal links of the carbon chain [12].

There are some discrepancies between different authors who describe positions of other lines that correspond to single-bond fragments and the chain of atoms bound by double bonds ($=\mathrm{C}=\mathrm{C}=$ $\equiv\mathrm{C}-\mathrm{C}\equiv$). In addition, in contrast to the line of 2100 cm^{-1}, the suggested positions of lines corresponding to aforementioned fragments in Raman spectra fall in the region where other bands exist, in particular, the bands of amorphous carbon and lines of carbon materials of mixed compositions, for example, [12]. And the line of 2100 cm^{-1} is set off in the spectrum on a nearly smooth background and suitable for recording and further analysis of results.

It turned out that Raman spectra are an effective tool to study and identify carbon chains. In [13] the length of LCC-chain has been calculated as a function of C-line position. In [14], on the basis of experimental data, a dependence has been derived that is somewhat different from the dependence found in [13]. Also, dependencies on chain length and type of terminal links were observed in other studies, for example, in [15,16].

One of the challenges in the synthesis and study of sp-carbon systems is their instability. For example, sp-carbon films are only stable in vacuum and hydrogen-terminated polyynes are stable within a limited time ($\leq$ weeks) and only in diluted aqueous solutions. Number of LCC links and their stability is limited by cross-linking reactions between chains and rearrangement of carbon atoms from the sp-hybridization with formation of sp^2-carbon or sp^3-carbon [15]. In recent years, it has been shown that a stable state of one-dimensional carbon chains can be achieved if terminal links are fixed on metal clusters [17,18].

In the case when neighboring atoms ($-$C$\equiv$C$-$) are vibrating in opposite directions, the vibration should be considered as an optical mode. At the same time, the dependence of vibration frequency on the length of fragment assumes a vibration propagating along the chain length and should be considered as an acoustic mode. Theoretical calculation of the optical and acoustic branches of the phonon spectrum has been made in [19]. Also, it has been found in this study that position of the C-line correspondent to optical oscillation should change to some extent depending on the length of carbon chains. Thus, the question about position of C-line and, perhaps, about its components requires further studying. Taking into account the fact that the line position could be affected by different factors, the problem is quite challenging. This defined the direction of further investigations in this study.

2. Samples and experiment technique

Samples for experiments on light scattering by carbon chains were produced in a single procedure with deposition of gold films. In [20] it has been shown that the process of thin films deposition used by us provides gold clusters with sizes close to each other (20$-$30 nm).

We believe that in this case accurate size of gold nanoparticles is not a decisive factor because in any reasonably expected case size and mass of carbon atom in a chain is much less than sizes and masses of gold particles. In our opinion, a more important factor is the distance between gold particles. This assumes that the carbon chain can be fixed on clusters on both ends. Such an assumption is consistent with results of DFT-calculations performed in [21], where it has been shown that carbon clusters on metal are more energetically favorable if they are secured on a plane.

To obtain samples with different distances between gold particles, films with a gradient of the gold layer thickness were produced.

Samples for experiments, the gold films with a gradient of thickness were deposited by magnetron sputtering with direct current on the gold target with a purity of 99.9 in a MCM-100 plant (South Korea) with pumping out by a backing vacuum pump to standard glasses for microscopic studies with a size of $76 \times 10 \times 1.2$ mm. Prior to the application of metal layer, the substrates were washed in isopropanol in an ultrasound bath with following washing by deionized water and drying in a drying cabinet.

The sputtering of gold was carried out in the atmosphere of residual air and argon with a purity of 99.9 at a pressure of $1-3 \cdot 10^{-2}$ mm Hg, a current of 40$-$70 mA at room temperature. The diameter of erosion zone in the target was 45 mm. The target-to-substrate distance was 19 mm. The magnetic system was made on the basis of Sm$-$Co permanent magnets. The sputtering time was 40$-$80 s. The gradient of gold layer thickness was provided by placing the substrates at different distance to the target and at different angles to the direction to geometrical center of sputtering. The range of distance varying was from 19 to 65 mm and the range of angles was from 0 to 70°. This provided variation of the thickness from the 10 nm-thick continuous film in the point opposite the geometrical center of the target to the nearly zero thickness in the most far point of the sample. Local thicknesses of different points of gold films were evaluated for specific samples proportionally to the thick reference film (more than 100 nm) applied under the same conditions and location of the substrate. Thickness and profile of the reference film were measured by a computer system based on a MII-4 interferometer.

The source of carbon in the discharge chamber was the vapor of ULVAC SMR-100 oil with the following parameters: chemical formula $(\mathrm{CH_2})_n$ $20 \leq n \leq 40$, vapor pressure at 25°C was less than $4 \cdot 10^{-1}$ Pa, density was $0.87\,\mathrm{g \cdot cm^{-3}}$, viscosity at 40°C was 50 cSt.

We believe that carbon structures in our cases could be formed initially in the atmosphere of electric discharge in the gas that filled the chamber. Many studies have confirmed the possibility of carbon structure formation from vapors in electric discharge [22–25]. In particular, in [23] it has been reported the formation of polyynes in a product formed in the discharge.

The scattering spectra were recorded using a HORIBA-JOBIN-YVON MRS360 modular micro-Raman spectrometer. The scattering was excited by a He$-$Ne-laser with a wavelength of 632.81 nm. For further details of the recording systems see [20,26].

3. Experimental results and processing (component separation)

As it has been shown in [26], the single-isolated line near 2100 cm^{-1} can be observed in our experiments in the Raman scattering spectra of thin island-type films of gold. The use of gold films different from each other was a flexible tool to study characteristics of the C-line, although it of course added an additional factor of uncertainty.

It was found in the experiments with films with gradient application of gold that indeed the intensity and shape of the line are related to the thickness of the gold coating. At this moment it is worth to note that sufficient intensity of the Raman emission in the region of 2100 cm^{-1} has been observed only in the case of films with the most insignificant thickness, i. e. the island-type, almost transparent films.

Based on the results of SEM and AFM from [20,26] a conclusion can be made that an individual cluster of gold in a film has the following dimensions: diameter of 20–30 nm and thickness of 1–2 nm. In the case of this evaluation in the sample region under the geometrical center of the target the film thickness of 10 nm is composed of 5–10 layers of clusters.

Fig. 1 shows dependence of the film thickness (curve *1*) and dependence of the Raman signal summarized over several samples (curve *2*) on the coordinate of point under study on the sample. The coordinate is defined as a distance between the projection of the geometrical center of the target onto the substrate holder and the point under study on the sample surface.

General behavior of the scattering intensity dependence is clear. At the edge of substrate far from the center of deposition, where there are no clusters in the extreme case, the signal intensity is below the detection threshold. As the film thickness increases, the signal grows and then decreases again. In the second case the decrease in intensity below the detection threshold can be easily explained by the fact that cluster are merged in a continuous film making unlikely enhancement of the signal due to the effect of surface-enhanced Raman scattering (SERS). Also, it is possible that continuous films are less effective for securing the carbon chains. Such a qualitative approach is all-sufficient to explain the observed behavior of the dependence of Raman signal amplitude on the position of measurement point on the sample.

The range of distances (from the center of the target being scattered) at which the Raman signal is observed for all studied samples in our case was from 50 to 57 mm. This range of distances has a correspondent range of film thicknesses from 1 to 0.7 nm. The intensity of Raman signal out of this range is below the noise level of the setup.

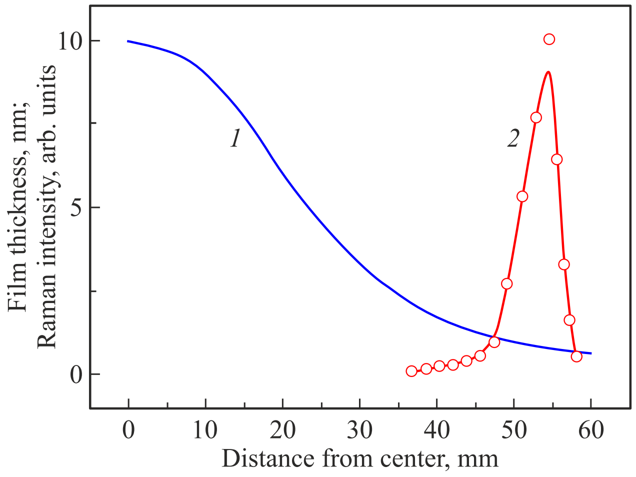

Figure 1. Dependencies of the gold film thickness (curve *1*) and the experimental Raman signal intensity (curve *2*) on the coordinate of measurement point on the sample.

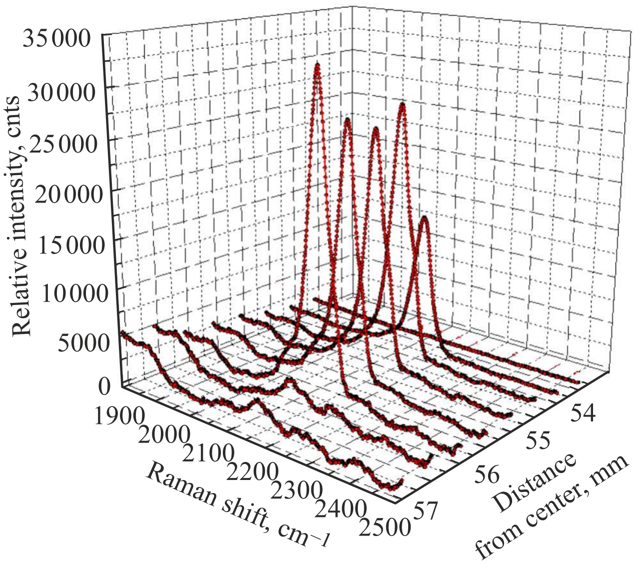

Figure 2. Profile of C-line in the Raman scattering spectra for a sequence of points on one of samples with thickness gradient.

The Raman scattering band in the region of C-line was inhomogeneous and had the form of superposition of a number of components. Fig. 2 shows spectra obtained from different points on one of the samples. The spectra shown in the figure were deconvoluted and their main components were identified. To preliminary extract parameters of the components, the software was used, which is attached to the HORIBA-JOBIN-YVON Ra.man spectrometer. The automatic determination of component parameters turned to be insufficient and further refinement was carried out by manual variation of component parameters. The refinement was conducted until coincidence between the experimental spectrum and the synthesized spectrum with an accuracy of up to the noise level of experimental curves.

Dependencies of intensities of these components on the position of measurement point on the sample differ from each other significantly. Band of the oscillation with lower energy (2145 cm^{-1}) has a quite sharp peak of intensity along the thickness gradient. In contrast, the intensity of component near 2170 cm^{-1} is the highest for the region with a coordinate of approximately 54.5 mm. This is also manifested on the integral characteristic of C-band intensity (Fig. 2), which has a sharp peak at the point with coordinate of approximately 55 mm. The 2080 cm^{-1} component also has its peak somewhat less manifested in the region near 56 mm, the same region where the 2145 cm^{1} line has its maximum.

The following figures show results of spectra decomposition into individual components. Fig. 3 shows dependence of spectral positions of individual components on the position of measurement point on the sample with thickness gradient

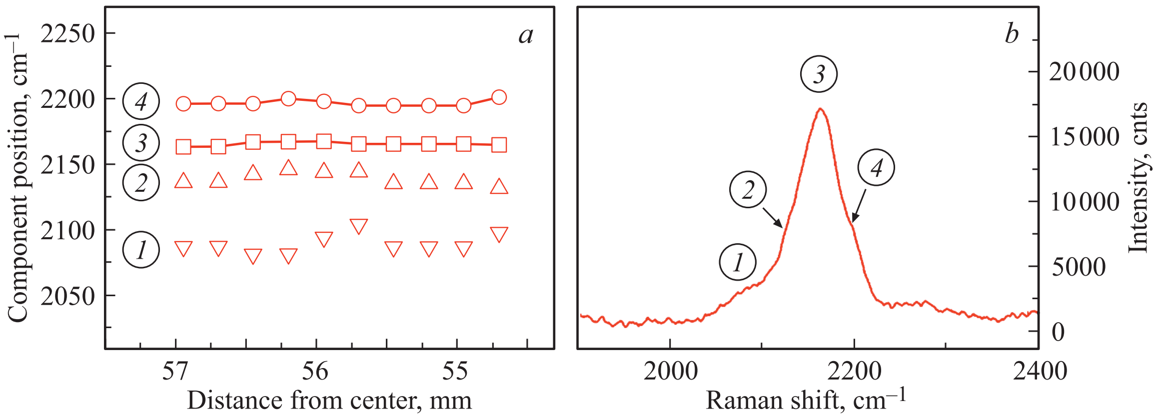

Figure 3. *a* — positions of individual spectral components of the C-line depending on the position of measurement point on the sample with thickness gradient; *b* — an example on integral spectrum on one of points on the sample with shown positions of calculated components.

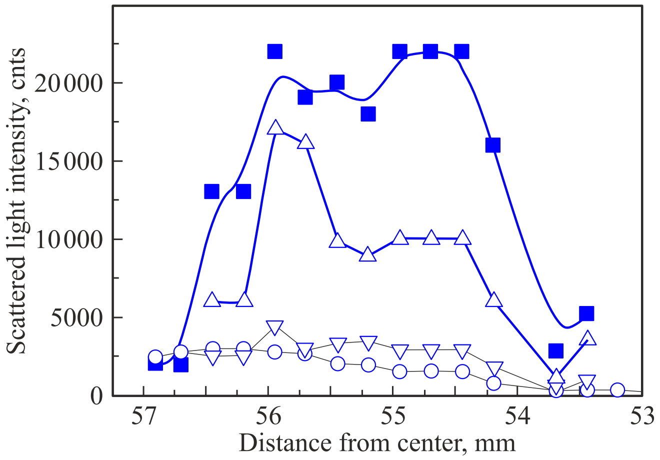

Figure 4. Dependence of the intensity of C-line components on the position of measurement point on the sample. Symbols correspond those used in Fig. 3.

(Fig. 3, *a*); Fig. 3, *b* shows an example of spectrum of the integral band with individual components indicated (foe one of points on the sample). The presented data is obtained for the approximation of experimental spectra by four the mostšignificant components. Fig. 4 shows dependence of intensities of C-line components on the same parameter.

First of all, It is worth to note that experimental spectra for different points on the gradient sample can de satisfactorily described by four components, which keep their spectral position almost unchanged throughout the entire sample. At the same time, the intensity of these components is dependent to a significant extent on the point in the sample where the spectrum is recorded. The spectrum is mainly formed by two intensive components near 2145 and 2170 cm^{-1}. Two other components provide a relatively low contribution to the C-line profile.

4. Discussion of results

First of all, It is worth to note that the existing studies of the Raman scattering by one-dimensional carbon chains and the dependence of line positions on the length have been performed with objects that are significantly different from those used in this study. Studies described in [14,16] and other studies have been performed with identified fragments of carbyne chains with chemical closure of terminal links. In our case the terminal links were not intentionally fixed and fragments were not separated along the length: subjects of the study were the formed carbyne fragments localized on islands of the deposited gold film.

The most unexpected result of this study is the combination of the stable spectral position of components (for points along the deposition gradient) and the sharp dependence of intensity of these components on the same factor. Also, factors that need explanation include the prevailing role of only two components in the formation of the integral line.

The combination of observed factors can be qualitatively explained within a model that consider the formation of carbyne fragments and their localization on clusters as not completely coinciding processes. In this context „not completely coinciding“ means that both processes are quite random and the formation of carbon chains can take place in the environment of electric discharge in gas and continue on the substrate. The existence of prevailing components instead of their continuous distribution over the length was found in [22,23], where the self-formation of a number of prevailing types of carbon fragments with specific lengths in electric discharge has been shown. (Additionally: in [22,23] the atmosphere of discharge was similar to that of our study: argon + hydrocarbon gas.) In [27] also fragments of carbyne with predominantly one size have been observed (TEM): 10–13 links. The fact that carbyne fragments can be formed in the atmosphere of discharge rather than anywhere else seems to be natural because the energy of discharge currents can provide the overcoming of necessary processes by the activation energy.

The dependence of intensities of components can be determined by different factors. As already noted, fragments that are localized on gold clusters on the substrate are quite stable [17,18]. This first of all provides for the existence of stable carbon chains, which signal is detected. This is confirmed by the fact that C-lines were observed in our experiments on the samples produced several months ago as well.

It is necessary to take into consideration, among other things, the intensity of the scattering line to be formed due to SERS. However, it should be taken into account that: SERS is a local effect; each cluster provides the emission enhancement in its immediate vicinity. If, as assumed, we observe a signal from carbyne fragments secured on gold clusters, then each fragment of the chain is secured on a pair of clusters, which provides for a certain general level of scattering signal enhancement for all secured fragments. Therefore, we assume that the SERS effect should have a weak influence on the profile of the integral scattering line.

It has been already assumed that the distance between metal clusters may be a significant factor that define lengths of carbon chains. Let us discuss it. It seems obvious that a fragment secured at two ends of the chain should be more stable as compared with that secured at one end. Moreover, such a fragment already has a fixed length and does not participate in the interaction through terminal links. In this case it is an oscillation system with a higher Q-factor, which should be manifested in a higher intensity and a narrow line in the Raman spectrum. To summarize: we will consider that the observed line is mainly contributed from the fragments secured at two ends on gold clusters.

Then the dependence of intensities of integral line components on the spectrum recording point on the sample can be explained at a qualitative level. In the region of the most thin film where the scattering just starts to manifest, the number of cluster is low and the mean distance between them is large. It means that the carbyne fragments deposited on the far end of the substrate may fail to find a point to secure or there may be no pairs of clusters at a sufficiently close distance.

For the points somewhat closer to the center of deposition the mean distance between pairs of clusters may be sufficient for securing on the pair of clusters, however, the mean distance between clusters is still relatively large. Chain fragments localized on such a pair of clusters have in average a relatively longer length. And, in accordance with the qualitative conclusions of [13–15], their correspondent component of the integral line is on the side of lower energies. As the film becomes thicker, the density of clusters increases, the mean distance between them decreases and the intensity of components with higher energies increases. This model allows explaining the behavior of curve family in Fig. 4.

Some additional qualitative considerations can be presented that characterize the relation of the film thickness to the intensity of the scattering signal. Assume the gold clusters are formed on the surface independently from the carbon component. Their density is proportional to the film thickness at the given point (however, the local distribution is random). The carbon chains are formed partly in the gas, but perhaps the formation (chain linking) continues on the surface followed by the localization on metal clusters. The main signal of Raman scattering is provided by the chains localized on gold clusters with both their ends. Then a region on the sample where distances between clusters are of the order of magnitude of the prevailing chain length will be the region where maximum signal of the certain component of the Raman scattering line is recorded. Previously references have been presented to different published studies that confirm validity of the assumptions made.

Now let us evaluate the distance between gold clusters on the basis of the available experimental information on the distribution of gold film thickness over the sample (Fig. 1).

With the assumed macroscopically regular arrangement of gold clusters on the substrate, the range of distances between clusters for a coordinate variation of $50-57$ mm is about $0-14$ nm depending on the assumption about the size of gold clusters.

The evaluations show that the observed maximum of the Raman scattering signal corresponds to the most probable lengths of carbyne molecules in the range of $5-10$ nm. It is a rather large distance compared to the length of the $C-C$ bond: single 0.154 nm), double (0.133 nm), triple bond (0.120 nm). Thus, the carbyne molecule (a hydrocarbon molecule that contain at least one triple bond) with the linear configuration must be composed of $33-65$ molecules of carbon. It is a rather large number, although TEM-images of long chains can be found in literature, for example, in [18]. The length of carbyne chain obtained in our evaluations can be resulted from the polymerization of pre-ionized $2-3$ molecules of oil vapor.

It should be noted once again that these considerations do not include the formation of carbyne fragments on the substrate itself. But this coincides exactly with the previously made assumption of the model where chain fragments can be mainly formed as early as in the discharge, in the gas, and with almost equal probability can be localized in any part of the substrate. This corresponds by default to the fact that the position of intensity peak of the Raman response depends only on the presence and arrangement of clusters.

5. Conclusion

Spectra are obtained for the Raman scattering in a region of $2100\,\mathrm{cm}^{-1}$ (C-mode) by one-dimensional carbon chains localized on thin island-type films of gold. A complicated dependence of the scattering intensity on the film thickness is found. Positions of individual components of the C-line are calculated with spectra recording in points with different thickness of gold films. The evaluations show that the region of peak intensity of components with lower energy (lower Raman shift) is in the region of a greater mean distance between the gold clusters, which is consistent with [13–15] and with our assumptions that components of the C-line correspond to different lengths of carbon chains localized on pairs of clusters with different distances from each other.

Conflict of interest

The authors declare that they have no conflict of interest.

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