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Inelastic light scattering by self-formed linear-chain aggregates of carbon atoms in gold island films

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The study of the optical response of gold island films revealed an intense line in the light scattering spectrum near 2100 cm^{-1}. Some possible reasons for the appearance of this line are considered. Comparison of the results obtained for films obtained by various technologies, light scattering spectra on other types of samples, as well as comparison with the results of other authors allow us to interpret the line as the result of inelastic light scattering by one-dimensional carbon chains.

Keywords: inelastic light scattering, gold films, SERS, one-dimensional carbon chains.

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1. Introduction

Unique properties of thin island films and nanoparticles of gold (AuNPs), silver (AgNPs), copper (CuNPs) attract close attention of researchers for the past 20 years. Photoluminescence of these metals was discovered in 1969 [1]. Gold and copper excitation was performed using a laser with the wavelength of 488 nm, and photoluminescence was observed near 564 nm (for gold) and 620 nm (for copper). Weak luminescence with a low quantum yield (QY) $\sim 10^{-10}$ was classified as an interband (d$-$sp) transition. Attention was not paid to this research area for a long time. The effect of enhancement of Raman scattering by a developed surface of a silver electrode was found in 1974 [2]. The phenomenon was called surface enhanced Raman scattering (SERS) and was widely used in chemical analysis, biochemistry and biology [3–9]. Possibilities to use gold clusters as optical probes in medicine is related to their inertness, which conditioned the active study of their optical properties. The study of SERS on Ag and Au films revealed a background radiation from the films of these metals, in addition to the typical spectral bands for organic materials. It was found that photoluminescence bands of gold films and nanoparticles (AuNPs) can be in a range from 400 nm to the near IR-region, depending on quantity of gold atoms in nanoparticles and their environment [5–8]. Thereat, QY of such nanoclusters was in $\sim 10^5 \div 10^6$ times greater than the one observed for the samples in [1].

The most intensive radiation is demonstrated by gold clusters sized from 20 nm to 0.3 nm, comprising from $\sim 10^6$ to several items. Brightly luminescent AuNPs are most often obtained by solution chemistry. The forming gold particles are close to the critical sizes of gold nuclei in the solution and are thermodynamically unstable, which leads to an even higher probability of their enlargement [10]. In order to stabilize the sizes, AuNPs clusters are surrounded by shells composed chiefly of various organic ligand molecules [9]. Most studies are carried out with such modified gold nanoparticles. The existing shells broaden the spectral lines and complicate interpretation of photoluminescence spectra. It is also impossible to ignore the influence of residual traces of reagents, involved in the formation of gold nanoclusters, on radiation spectra. Therefore, despite a large number of studies, the nature of AuNPs glowing is still not completely clear.

The authors of [11] obtained island gold films on copper substrates by the magnetron sputtering method. The surface of the obtained gold films was studied by scanning electron microscopy. The films had the form of a layer of gold particles (approximately spheroids) $\sim 30-40$ nm. When exciting these gold films by a He$-$Ne laser (632.8 nm), the authors found an intensive and narrow radiation band near 733 nm. The band width was ~ 0.016 eV, which is by more than an order lesser than the typical luminescence band widths observed in AuNPs in solutions. The said spectrum band was also observed for the samples stored for a long time (more than a year). It should be noted that the obtained gold nanoparticles did not have artificially created stabilizing shells.

The present paper was initially aimed at revealing the nature of radiation of shell-less gold nanoclusters being on the surface of various substrates.

2. Experimental procedure and sample preparation

The samples for experiments — gold films of different thicknesses were deposited by cathode or magnetron sputtering onto various substrates. Colloidal gold dried from aqueous solutions was also used in the experiments.

The substrates were the standard microscopy glasses, silicon plates, and copper and aluminum foils in certain experiments. A copper or aluminum interlayer was also applied in some cases on a glass substrate, prior to gold sputtering. Metal layers of copper and aluminum were applied by electron beam evaporation using the STE EB 48 unit at 140–1500°C in basic vacuum not worse than $1 \cdot 10^{-6}$ Pa. The Cu and Al layer thicknesses were 100 and 150 nm. Vacuum during sputtering was approximately 10^{-5} Pa, increase rate was $0.5{-}0.7\,\mathrm{nm} \cdot \mathrm{s}^{-1}$.

A gold layer was applied by cathode and magnetron sputtering of a gold target with the frequency of 99.9 using MCM 100 and VUP-5 units at room temperature. A gradient of gold layer thickness was intentionally created in a part of the samples. To do so, we placed the substrates at a different distance from the geometric center of target sputtering. Thereat, thickness changes from almost 0 to a solid film 40 nm thick were obtained. Average thicknesses of particular samples in the area of optical properties measurement were determined by calculation, based on the known sputtering rate.

The object of some experiments was the dried colloidal particles of gold. A sample for experiments in this case was prepared as follows: a drop of pink aqueous solution of colloidal gold was dried in air on a glass or a polished metal substrate. The drop dried and formed a noticeable trace along the external drop edge. Such a profile of the dried drop trace is a result of capillary flows and the mechanism of this phenomenon is known [12].

Optical experiments with inelastic light scattering were performed using a modular HORIBA-JY MRS320 micro-Raman spectrometer, with excitation by light of a He–Ne laser with the wavelength of 632.81 nm with an OLIMPUS BX41 microscope. The main array of spectra was obtained using the MPlan N 50/0,75 lens. The experiments were performed at room temperature.

The relief of the films under study was studied using the following: Integra Aura atomic-force microscope (AFM) (NT-MDT), intermittent contact mode, HA_NC_A cantilever oscillating at the resonance frequency of 224 kHz, amplitude of free and operating oscillations being 20 and 15 nm.

3. Results

The main experimental result obtained in this paper is a narrow band in the spectrum of inelastic light scattering on thin island gold films and colloids. As already noted, the authors have observed a similar band in the region of about $2100\,\mathrm{cm}^{-1}$ ($\sim 720{-}730$ nm) for the first time for two-layer copper–gold films [11]. (The „film“ notion will be used as a common term for a deposited material, both for solid films and for limit thin ones consisting of individual clusters.) Our study was performed on a large array of samples on different substrates, which allowed for a detailed study of the effect.

In a new series of experiments, the discussed band was observed on most samples. First of all, the experiments have revealed that the band is observed in the gold film glowing spectra applied on different substrates — glass, copper, aluminum, silicon. Its intensity on relatively thick (solid) films is considerably weaker — by one and a half-two orders. The band position varied insignificantly depending on application technologies and substrate type. The reasons of instability will be discussed later. Band intensity might depend on the sample point where the spectrum was taken which appears to be due to insufficient uniformity of sputtering . The glowing band position for gold films applied on aluminum, silicon or glass substrates might differ insignificantly (by $10{-}20\,\mathrm{cm}^{-1}$). The glowing band of the samples with gold sputtered on a copper interlayer was noticeably further away from the excitation line. An additional shift of the band in the spectrum of these samples (in relation to the band position for samples with a glass or aluminum substrate) was $20{-}30\,\mathrm{cm}^{-1}$ (about ~ 3 meV or ~ 1 nm). This position different in certain experiments was up to $70{-}80\,\mathrm{cm}^{-1}$ (towards longer waves), Fig. 1 and 2.

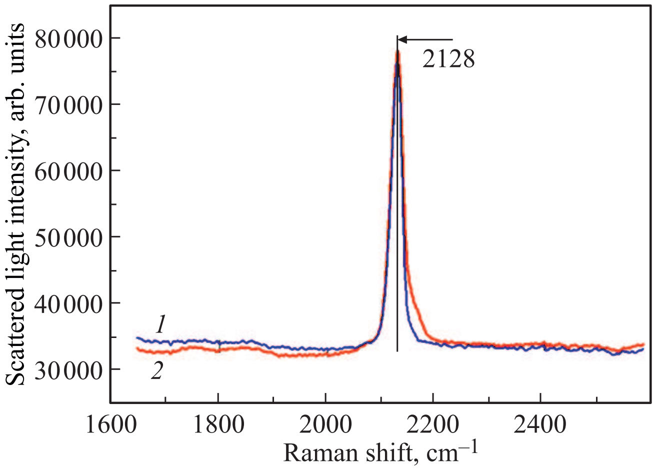

Figure 1. Spectra of light scattering by an island gold film on glass in the region of $1600{-}2600\,\mathrm{cm}^{-1}$. *1* — scattering spectrum in the film region ~ 3 nm thick; *2* — scattering spectrum in the film region ~ 5 nm thick. The spectra are normalized by the maximum.

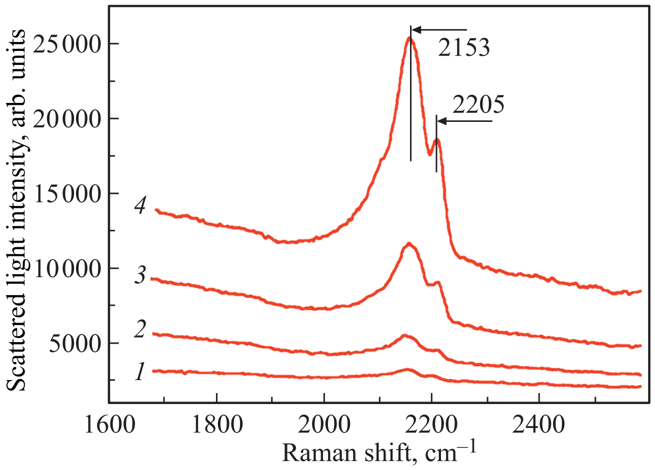

Figure 2. Spectrum of light scattering by an island gold film on a copper interlayer. The calculated gold film thicknesses for curves *1, 2, 3, 4* are 35 nm, 15 nm, 7 nm, 3 nm.

Let us consider the optical experiment data. The band shown in Fig. 1 is the glowing spectrum of the thin gold film $\sim 3-5$ nm thick on a glass substrate. Thicker films have a slight widening of the band from the side of greater Raman shifts.

The band position in the gold spectra, on substrates with a copper interlayer, was characterized by a greater spectral shift in relation to the excitation line (632.8 nm). The band width for these samples was considerably larger. Band half-width (FWHM) for the samples with a copper interlayer reached $150-200\,\mathrm{cm}^{-1}$, while for the films applied on glass there were considerably narrower bands, with a half-width of $20-30\,\mathrm{cm}^{-1}$. The main line in some cases was accompanied by a weak satellite with a greater Stokes shift. The samples sputtered on a copper interlayer had quite a resolvable spectral doublet. Experiments were also performed with gold colloids obtained from aqueous solutions. The result in these experiments — a band present in the spectrum — depended on method of gold colloid solution preparation. A band was observed when the colloidal solution was prepared by the standard citrate method [13]. The appearance of the edge of the dried drop of colloid solution, prepared by the citrate method, and the spectrum of the observed band are shown in Fig. 3, *a, b*. The microphotograph shows that the drop trace edge is non-uniform: large and small particles settled during drying in different areas of the edge trace. However, the band under discussion was not observed in a similar sample, when a colloidal solution prepared using inorganic reagents was used. The revealed dependence of band occurrence in the spectrum on colloid preparation method will be discussed later.

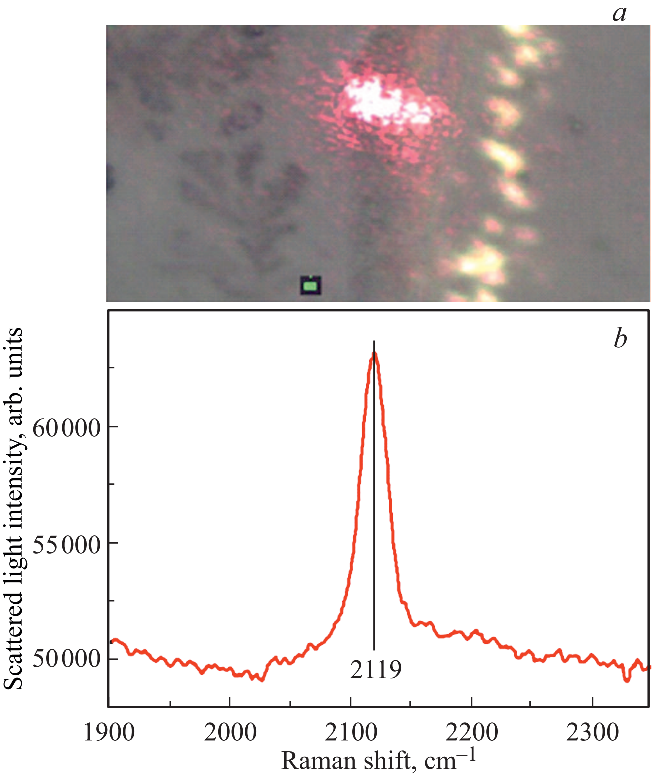

Figure 3. *a* — microphotograph of the edge of the dried drop of colloidal gold solution. A pure substrate is shown in the figure on the right, behind the bright band. The horizontal size of the scale bar is 1.8 μm. The drop edge contains several sediment layers; the brightly lit ones are large gold particles. The laser exciting the glowing is focused on the left, on the dark band; *b* — spectrum of inelastic light scattering from the drop trace in the region of $1900-2300\,\mathrm{cm}^{-1}$.

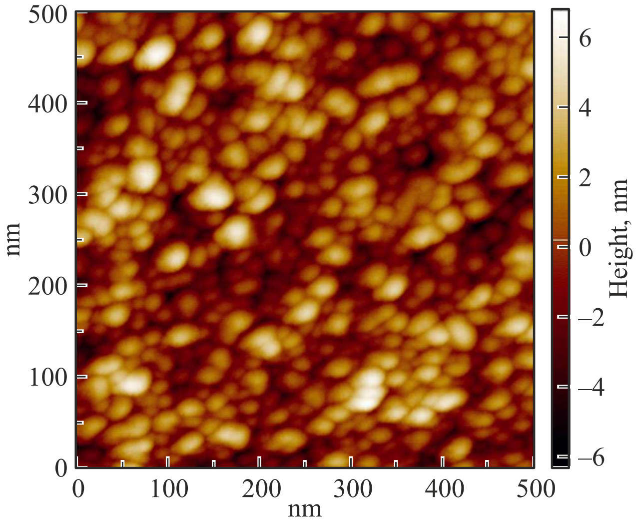

Figure 4. AFM-image of the surface of the gold film applied on a glass substrate. The scales are given in the figure.

The structure of the sputtered film can be judged by the surface profile shown in Fig. 4. The figure shows that the film, obtained in our conditions, consists of individual gold granules (clusters), sized from 10–30 nm. A more precise determination of cluster sizes is limited by the AFM microscope resolution power. The noted island nature of the film is essential for understanding the study results. For a more justified subsequent analysis of the obtained data, we also recorded the film glowing spectra in a wider range of energies. Fig. 5, *a, b* also shows such spectra in the range of Raman shift of $100-2750\,\mathrm{cm}^{-1}$ from the excitation line. It is seen from the spectra that, though the line $2100\,\mathrm{cm}^{-1}$ is the most noticeable spectra detail in this range, other lines are also present. This data will be analyzed and interpreted in section „Discussion“.

4. Discussion

The authors analyze and interpret the data on the assumption that the narrow glowing bands, observed in the region of $2100\,\mathrm{cm}^{-1}$ in the scattering spectra of different gold film samples, have the same object conditioned by the same reason in all cases.

The unusual properties of the observed glowing, in the first place, pose the question of whether this observation is an experiment error.

The discussed band was observed only on the samples with a gold film. The band was not observed on any other samples. Check experiments with the samples were performed on two other units. The line on one of them was observed under excitation similar to our excitation — by light with the wavelength of 632.8 nm, and was not observed at the excitation length of 514 nm either in the region of 2110–2150 nm^{-1} or in the region near 720–730 nm (supposing it was luminescence). Weak traces of the line 2160 cm^{-1} were observed on another unit under the 532 nm excitation on the sample with a copper interlayer. Thus, the noted glowing is not an experiment error.

Further analysis requires determining the band nature: whether the observed glowing is luminescence or whether the spectrum line corresponds to inelastic light scattering. The available data gives an unambiguous answer to this question. Such a narrow width of the observed band is not typical for luminescence, and is typical for Raman spectra. Moreover, an experiment with excitation by light with the wavelength of 532 nm showed a weak maximum in the region near 2100 cm^{-1}, and did not show the band in the region of 720–750 cm, as in the case of luminescence. Thus, the observed narrow band is a manifestation of inelastic light scattering.

A more complex question is — what generates the observed band? Raman scattering in metals, as far as the authors know, was not observed. Even if we recorded Raman scattering in the metal due to some reasons, its frequency would be much lower in terms of energy due to the large gold atomic mass. Therefore, the discussed line cannot be associated with Raman scattering directly in gold. A certain substance that provides the band in the scattered light spectrum must form during gold film formation.

Though gold is usually considered a reference of chemical inertness, it can oxidize, including the medium of an electric discharge in a gas — i.e. in the conditions used for its sputtering in our case. Two types of gold oxides $\mathrm{Au_2O}$ and $\mathrm{Au_2O_3}$ are known [14,15]. Some parameters of these materials are calculated in [16]. Based on the results of [16] both oxides are semiconductors with a band gap slightly less than 1 eV. This is another reason why the discussed band cannot be luminescence of the oxides formed on the gold surface.

Paper [16] also gives the calculated vibrational modes for the above-mentioned oxides. All the vibrational modes of the lattices of these oxides are below 500 cm^{-1}. This confirms the above-mentioned evident considerations that compounds of heavy elements cannot have lattice vibration modes in the region of 2100 cm^{-1}. Consequently, the discussed band must correspond to inelastic scattering on the substance which forms during the making of Au films.

It should be also noted that weak lines manifest themselves rather steadily in the region of 300–500 cm^{-1} in the obtained spectra (Fig. 5, *a*, *b*), which can be a manifestation of scattering, but this is not a subject matter of the present paper.

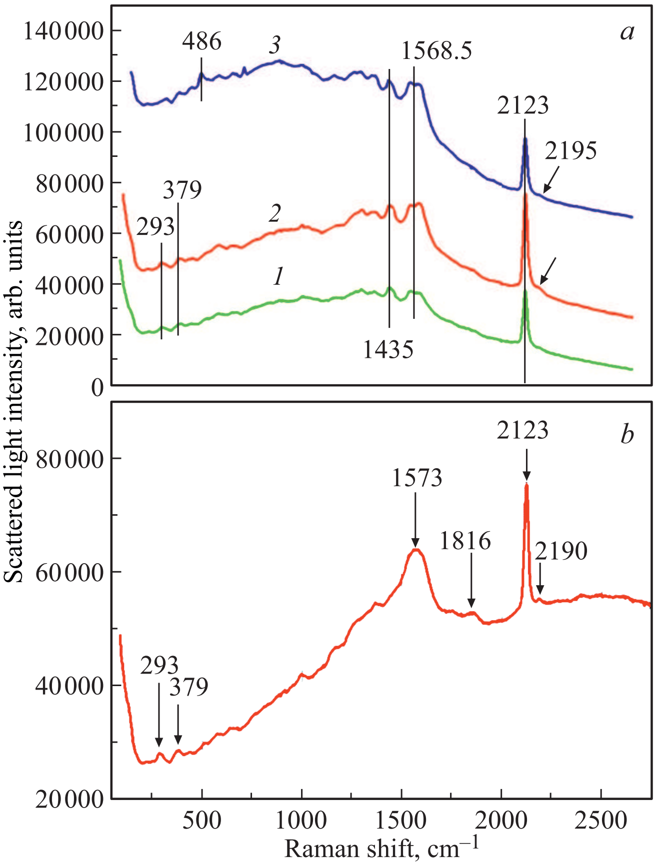

Figure 5. Spectra of inelastic scattering from a thick film (40 nm) (*a*) and (*b*) a thin film (3–5 nm). The weak line near 2123 cm^{-1} is marked with an arrow. Discussion in the text. The three spectra in Fig. 5, *a* are from different points of the sample. The spectra are separated vertically for better perception.

An analysis of the available publications has revealed that lines close to 2100 cm^{-1} can be observed in case of light scattering on molecules of carbon monoxide CO, as well as in case of scattering linear carbon chains with the **sp** configuration (carbynes). Both substances might form during gold film sputtering. The necessary oxygen for CO formation might be present in the sputtering chamber as a residual gas. The necessary carbon for both materials light form upon destruction (in an electric discharge) of vacuum oil vapors from the evacuation system. The closeness of the band positions in the CO and carbyne spectra is due to the fact the line in both cases corresponds to vibrations of atoms bound by a ternary chemical bond $-\mathrm{C}\equiv\mathrm{C}-$ and $\mathrm{C}\equiv\mathrm{O}$, whiles masses of vibrating atoms in this case are close. The fact that carbyne chains (on a substrate) may form under an electric discharge in a gas has been confirmed experimentally in [17].

Let us consider the reasons why the discussed band in the spectrum cannot pertain to CO molecules. First of all, CO content in atmospheric air is small $(0.01-0.05 \cdot 10^{-3}\,\mathrm{g/m^3})$ and it makes sense to discuss the possibility of scattering by molecules adsorbed on the surface. CO molecules, in principle, might form in an electric discharge in the presence of vacuum oil vapors and residual oxygen. However, the temperature of CO desorption from the gold surface is below 200 K [18] (this value differs for different crystal planes, the maximum figure is given here). Paper [19] shows that CO traces on the surface of an island gold film at room temperature disappear within approximately 10 hours. The discussed line in our experiments was also detected in samples stored for more than a year. Finally, the line in the sample spectra obtain in an argon medium (i.e. without oxygen) was detected with approximately the same rate as in the two previous experiments. All this makes it possible to exclude scattering on carbon monoxide molecules as a possible interpretation variant.

In addition, another experimental fact excludes the interpretation of the discussed line as a manifestation of scattering on CO molecules, while speaking in favor of the hypothesis of scattering in linear agglomerates of carbon. The above-mentioned variability of the position of this line in the spectrum cannot correspond to scattering on a CO molecule. This is a relatively simple molecule having one vibration mode [20,21] frequency of which must not depend on external factors. The more so, we see no reason of possible occurrence of splitting and formation of a doublet in the spectrum (Fig. 2). We think that this is an unambiguous argument to confirm our interpretation of the experiments.

At the same time, it is known that the vibration frequency of the $-\mathrm{C}{\equiv}\mathrm{C}-$ fragment, which is near the position of $\sim 2100\,\mathrm{cm}^{-1}$, must depend on several reasons: on chain length and on the method of linear chain closure [22]. Apparently, frequency can be also affected by a possible branching from an irregular carbon atom in the chain. Thus, in addition to excluding the alternative interpretations, the noted line position variability unambiguously points to a linear chain of carbon atoms as a source of the $2100\,\mathrm{cm}^{-1}$ line in the scattering spectrum.

We cannot yet unambiguously indicate a second line that must manifest itself in carbyne spectra. The $\sim 2100\,\mathrm{cm}^{-1}$ line corresponds to a vibration of a ternary bond in the $-\mathrm{C}{\equiv}\mathrm{C}-\mathrm{C}{\equiv}\mathrm{C}-\mathrm{C}-$ carbon chain. But such a chain must also contain a line that corresponds to an ordinary bond. This line, according to various publications, can be located in the region of $(1100-1600\,\mathrm{cm}^{-1})$, which is in the amorphous carbon band range. Moreover, the line that corresponds to vibrations of an ordinary bond must be significantly weaker than the line of a ternary bond [22–24]. The obtained spectra (Fig. 5, *a, b*) in the specified region have bands which are close to the $\mathbf{sp}^2$ band of graphite (but they evidently wider than the crystalline graphite bands). The said spectral region also contains several other bands which cannot be unambiguously interpreted, but which can correspond to an ordinary $\mathrm{C}-\mathrm{C}$ bond in a carbon chain.

The experiments with dried colloids, despite their being of a different nature, also indirectly confirm our interpretation. The discussed $2100\,\mathrm{cm}^{-1}$ line must correspond to vibrations of the $-\mathrm{C}{\equiv}\mathrm{C}-$ fragment. The reaction products during gold making by the citrate method contain such fragments, and such fragments are absent when inorganic reagents are used [13]. This is another experimental confirmation of our interpretation.

It is not quite clear why sputtering on copper leads to a considerably different position of the band; in what does this differ from other cases? It can be supposed that copper, being rather an active material, somehow affects the nature of the process of carbon structure self-formation.

Finally, the role of gold has still not been considered in the discussion. In our opinion, gold plays a twofold role. The important role of gold is to provide a possibility to observe scattering from the ultimately small quantities of linear (carbyne) carbon chains. As has already been mentioned, gold is an efficient material to enhance the signal of surface light scattering (SERS) [2]. The importance of this mechanism in our case is confirmed by the observed inverse dependence of scattering signal intensity on film thickness — the signal was the minimum on the thickest film part where the gold was sputtered in a continuous layer.

Moreover, account of gold role due to enhancement by the SERS effect agrees with the revealed signal dependence on excitation light wavelength. Paper [25] analyzes the relation of the real and imaginary parts of dielectric susceptibility of gold at optical frequencies. The authors conclude that enhancement must be the most efficient in the range of approximately 600 nm. This agrees with the results of our experiments with excitation of glowing by light of different wavelengths.

Gold, apparently, also plays a structural role, in addition to optical enhancement. Paper [23] states that gold clusters may act as efficient terminal links during self-formation of carbyne chains and thus stabilize them. This issue is considered in more detail in [26] which gives the models of carbyne chain stabilization on the transition metal surface, gold in particular. This is another possible factor of substrate metal type influence on the results of our experiments.

5. Conclusion

Thus: we studied inelastic light scattering in island gold films and found a narrow band in the spectra near $2100\,\mathrm{cm}^{-1}$. An analysis of the obtained data for a wide range of samples and a comparison with literature data made it possible to identify the observed line as a Raman scattering line corresponding to oscillations of carbon atoms in linear $-\mathrm{C}{\equiv}\mathrm{C}-$ chains.

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Conflict of interest

The authors declare that they have no conflict of interest.

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