Study of nanocarbon thin-film field-electron emitters by Raman spectroscopy

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Abstract. Raman spectroscopy was used to study the features of the electron-phonon interaction in thin carbon films that are capable of low-field emission of electrons. It was found that in the Raman spectra of samples with this ability the characteristic peaks of carbon were almost completely suppressed, and also a wide photoluminescence band could be present. At the same time, the Raman spectra of non-emitting samples had the form typical of graphite-like carbon spectrum. This observation is in accordance with the two-barrier model of low-field electron emission from thin films of considered type, corresponding to which their emissive capability is maintained by the presence of hot electrons. Thus, in thin films consisting of numerous isolated carbon islands (nanoclusters) the extraction of electrons into the vacuum is facilitated by prolonged hot electron lifetime. Such prolongation, in turn, can be associated with the suppression of electron-phonon interactions by the spatial confinement effect. Consequently, it should result in the decrease of prominent bands in Raman spectra which are originated by electron-phonon interactions, while the photoluminescence intensity may, on the contrary, rise. Particularly such deformations of the Raman spectra were observed in the present study.

1. Introduction
Cold field emission sources of electrons have obvious advantages over thermionic cathodes, such as higher energy efficiency and short turn-on time. With the advent of cold cathodes based on carbon nanotubes (CNTs), the area of practical use of the field emitters has considerably expanded. However, some inherent problems of the CNT-based cathodes, such as emission current instability and insufficient lifetimes [1, 2], determine the increasing researchers’ interest to possible alternatives, for example, based on nanolayered [3-5] or other nanostructured materials.

Different varieties of carbon films are known [6-14] to be able to produce electron emission under external electric fields of low macroscopic intensity (of the order of 1 V/μm or less). Remarkably, this ability may be exhibited even by material and structures obviously failing to meet the two basic requirements of the classical Fowler—Nordheim emission theory, i.e., low work function of the material and/or presence of sharp surface protrusions. Further improvement of carbon film cold cathodes with relatively smooth vacuum boundaries [8-10] and their practical implementation are hindered by the lack of the knowledge on the mechanism of field emission realized in their case.
Previous works [14-16] presented the results of experimental studies of low-field electron emission from thin films of graphitic carbon. The films were deposited on doped monocrystalline silicon wafers and had effective thickness as low as 1–3 nm. It had been established that discontinuous (nanocluster) films can possess high emission capability. This led to the suggestion [14-17] that the mechanism of the observed emission involves generation of hot electrons as its required stage. In this context, the emission might be additionally promoted by increased hot-electron lifetimes in graphitic-carbon nanoclusters. Such increase is known to result from suppression of electron-phonon interaction by the electron localization effects. Their influence on the electronic structure, carriers dynamics and interactions in nanosized systems, as well as associated with such effects phenomena (e.g. photoluminescence), have been considered in numerous studies [18-23]. This work pursued the purpose to verify this hypothesis using the Raman spectroscopy method – as the suppression of electron-phonon interaction was expected to manifest itself in Raman spectra, in particular, by reduction of the features characteristic for graphic carbon [24-26].

2. Experimental Methods and Samples

The carbon film samples used in the reported work had the same structure, parameters and origin as in the previous experiments [15, 16]. They were provided by S.K. Gordeev and his group of the Central Research Institute for Materials (St. Petersburg). Carbon films of the required nanometer-scale effective thickness were deposited onto naturally oxidized p-type silicon wafers by CVD deposition from acetylene-containing gas mixture at elevated temperatures (730-760 °C).

Wafers with different crystallographic orientation were chosen. Two of them had densely packed surface facets, namely, (111) and (100). The third one was cut at 4° with respect to (100) plane. As it had been shown in [16], the utilized CVD process allowed the manufacturer to deposit carbon films of nanocluster (island) morphology on dense faces – in accordance with the Volmer-Weber film growth mechanism. On the wafers cut at (100)-4°, continuous carbon coatings formed.

As expected from previous experiments [16], the films grown on close-packed surfaces (111) and (100) had the capability of low-field electron emission: the corresponding current-voltage characteristics are shown in figure 1. The sample on the (100)-4°-oriented wafer did not emit any measurable electron current in macroscopic field up to 5 V/μm.

![Figure1](image-url)

**Figure1.** Current-voltage characteristics of carbon films on densely packed silicon surfaces measured in flat geometry with 0.6 mm distance between the sample and a 6 mm²-area round anode top.
One more carbon film sample was fabricated on a substrate partially subjected to chemical etching to form the so-called "porous silicon" [27] with high concentration of structural defects; the rest of the substrate remained unprocessed. Carbon film was deposited on both the etched and the virgin parts of the sample in the same CVD process. Comparison of film properties at different spots was intended to confirm the noted correlation between defectiveness of the substrate and morphology of the deposited film.

Raman spectra were recorded at room temperature with the use of Horiba Jobin-Yvon LabRam HR800 instrument in the backscattering geometry. Wavelength of its excitation laser (Quantum Torus) is 532 nm; the grating has 1800 grooves per millimeter. The incident beam is focused onto 2 µm sample surface spot with a 50x objective. Data acquisition was carried out in the frequency range corresponding to the Raman shift from 100 cm\(^{-1}\) to 7000 cm\(^{-1}\) in two modes: within 20 seconds with averaging over 20 measurements, or within 10 seconds with averaging over 10 measurements.

3. Results and Discussion

Figures 2–4 present Raman spectra for a few different surface spots on each of the studied samples. Figure 2 shows the Raman spectra for the film formed on a (100)-4°-oriented substrate, which were all similar. The peaks near 520 cm\(^{-1}\) and 950 cm\(^{-1}\) are characteristic for silicon [24]; the grating has 1800 grooves per millimeter. The incident beam is focused onto 2 µm sample surface spot with a 50x objective. Data acquisition was carried out in the frequency range corresponding to the Raman shift from 100 cm\(^{-1}\) to 7000 cm\(^{-1}\) in two modes: within 20 seconds with averaging over 20 measurements, or within 10 seconds with averaging over 10 measurements.

Raman spectra for dense silicon faces (which were capable of low-field electron emission) had fundamentally different character (figure 3). The peaks which are characteristic for graphite-like carbon had small heights close to or below the noise level. At the same time, a majority of such spectra included wide luminescence bands with magnitudes, shapes and positions varying from spot to spot and from sample to sample.

The observed difference in the magnitudes of carbon-related features in Raman spectra for emitting and non-emitting samples was in line with expectations. It witnesses in favour of the hypothesis [17]
about relationship between the mechanism of low-field emission by island carbon films and increased hot-electron relaxation time resulting from electron-phonon decoupling in nanosized domains. Photoluminescence is, in principle, uncharacteristic for graphite-like carbon as a material with no band gap. Its appearance in our case, together with dramatic reduction of “normal” features of Raman spectrum for graphitic carbon, can be considered as a sign of suppressed electron-phonon interaction which often serves as the most effective channel of non-radiative relaxation of hot electrons. At the same time, the carbon nanodots (nanoclusters) are known to show high photoluminescence capability [29-32]. The observed variations in the luminescence spectra for different spots of the studied films is in good agreement with high non-uniformity of emission current distributions recorded in previous experiments [14, 16].

Figure 3. Fragments of Raman spectra for carbon films on the substrates with surface orientations (111) – A1 and A2, left axis; and (100) – B1 and B2, right axis). The arrows indicate the expected positions of D and G peaks for graphitic carbon.

Raman spectra for the carbon film deposited on the partially etched silicon substrate are shown in figure 4. The spectra for the untreated area where the substrate surface retained high crystalline quality provide no evidence for the presence of carbon. Nevertheless, its presence had been revealed by other methods. In particular, under optical illumination this area showed pronounced photoconductance property; its characteristics are presented in figure 5. According to previous data [15], the photoconductivity phenomenon for the studied carbon films correlates with their high emission capability – both presumably requiring film discontinuity. It must be noted, however, that we had not performed any emission tests for this specific sample, and the absence of the luminescence bands in Raman spectra in figure 4(a) may be associated with this fact – if we assume that the luminescence capability of the studied carbon films appears simultaneously with the capability of low-field electron emission. In many previous experiments [14] extraction of a measurable emission current required preliminary annealing of samples in vacuum. The sample deposited on a partially etched Si substrate had not been subjected to such procedure.
Figure 4. Raman spectra for the carbon film sample formed on a partially etched Si wafer: (a) untreated region; (b) etched region (carbon film on porous Si). The inset in 4(a) shows a SEM-image of the corresponding carbon film, its island-like morphology is notable.

Raman spectra for the carbon deposited on porous silicon (figure 4(b)) also have a number of noteworthy features. Among them are the well-pronounced peaks denoted as “G”, “D” and the band “2D” (2500...3500 cm⁻¹) and associated with graphite-like carbon. High magnitudes of these features, especially in comparison with the reduced Si peak at 520 cm⁻¹, witness that, as expected, high substrate defectiveness led to formation of a continuous carbon coating. This conclusion is additionally supported by low electric resistivity of the film in the etched-substrate region (of the order of 10⁻³ Ohm·cm), practically unaffected by optical illumination. Moreover, the considered Raman spectra (figure 4(b)) include a broad luminescence component covering almost the entire displayed wavenumber interval. In this case, we attribute the luminescence to porous silicon [15, 33], the study of which is beyond the scope of this work.

Figure 5. Characteristics of the surface conductivity of the carbon coating formed on the untreated region of the substrate.
4. Conclusion
The study of Raman spectra of thin carbon films deposited on silicon substrates by the CVD method revealed a correlation between their ability to produce low-field electron emission and decreased intensities of the spectral components related to lattice vibrations of graphite-like carbon. This agrees with the previously suggested emission model assuming involvement of hot electrons in the emission mechanism. Another finding of the performed work consists in observation of photoluminescent ability (more or less pronounced) of the films with the best emission properties. Further studies might be aimed onto detailed investigation of spectral characteristics of this photoluminescence and its decay times, presumably reflecting electron state distributions and hot carriers’ dynamics in the centres of low-field electron emission from carbon cluster films.

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