STS study of nanocarbon films on oxidized silicon

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Abstract. Carbon cluster coatings deposited on oxidized silicon are known to possess the capability of low-macroscopic-field electron emission. Also, such films show anomalous photosensitivity of their electric properties. Though, physical mechanisms of both these phenomena remained unclear. New experimental investigation of such coating was performed by means of scanning tunneling microscopy and spectroscopy under varied optical illumination. Its results witness in favor of hot-electron mechanism of the low-field emission capability showed by the studied cluster films.

1. Introduction
In comparison with the more commonly used thermionic cathodes, cold cathodes utilizing the phenomenon of electron fields emission possess a number of inherent advantages, such as low energy consumption and short turn-on time. These benefits are becoming more and more decisive for modern applications. The immediately emitting elements of the field-emission cathodes most commonly represent metal tips, carbon nanotubes or fibers, etc. [1-13]. These elements concentrate the applied electric field, so that field enhancement factor as high as $\beta \approx 1000$ is achieved. As the result, emission current can be extracted in very moderate macroscopic field $F$ (of the order of V/µm) – if the latter is estimated by the ratio of the applied voltage to the field gap width. However, many different species of electrically heterogeneous carbon materials with relatively smooth surface (incapable to produce high geometric field enhancement) are also known to have the property of cold low-macroscopic-field electron emission [13]. Emission mechanism responsible for this property remains unclear [14].

Previous studies performed in our laboratory [15, 16] have demonstrated that thin carbon cluster films (with effective thickness of the order of a few nm) deposited on Si wafers can emit electrons at $F < 1$ V/µm at room temperature. The same films also showed relatively high photosensitivity [15], sufficient to consider their possible implementation in optical sensors. Having nm-scale thickness, the developed emissive films allow comprehensive investigation with surface-sensitive experimental techniques. In this paper, we present the results of their investigation by means of scanning tunneling microscopy (STM) and spectroscopy (STS) methods.

2. Sample and experiment
The reported STM/STS investigation of local surface conductivity and density of electron states (DOS) near the Fermi level was performed for one of the carbon film samples on p-type Si substrates from the series which had been previously studied in [15, 16] and showed ability to emit electrons in macroscopic electric field $\sim 1$ V/µm. Vacuum tunneling microscope SMM 2000Vac (by Proton-MIET, Russia) was used.
The measurements were performed in vacuum not worse than $10^{-5}$ Pa. First, STM images of the surface were recorded. Then, DOS functions were measured for several points on the imaged area using the following procedure. The microscope feedback was disabled and I-V dependencies of the tunneling current \( I(U) \) were measured for a fixed distance between the microscope probe and the film surface determined by the “tip approach parameters” \( U_0 \) and \( I_0 \). Then the distance was reduced and the \( I(U) \) measurement was repeated until it became independent from the “tip approach parameters”. For such distance, we considered the effective resistance of the tunneling gap to be negligible in comparison with resistance of the sample. Theory states that in this case the derivative \( dI/dU \) reflects the DOS function of the characterized surface. Each \( I(U) \) plot was recorded in ca. 500 ms. No less than ten such plots were recorded and averaged for each probe position to reduce the effect of current fluctuations. The optimal “tip approach parameters” were found to be \( I_0 = 1 \) nA, \( U_0 = 1 \) V.

As the characterized films were photosensitive, the surface topography measurements were performed in the dark to exclude photocurrent (having only a weak dependence from the probe-surface distance) from the probe current signal. Later, the effect of optical illumination (ambient laboratory light) on the \( I(U) \) plots was also tested.

3. Results and discussions
Figure 1 presents a typical STM image of the studied carbon cluster film on \( p^+\cdot Si \) wafer recorded in the “\( I = \text{const} \)” mode. The acquired surface topography is in good agreement with previously obtained AFM data [15, 16] but gives more fine details due to much better lateral resolution provided by the STM method.

The measured tunneling \( I-V \) curves (or integral DOS functions) were different for different probe positions (figure 2). They may be classified into three main groups. The plots of the first group were measured at topographic recessions. They show band structure of the \( p \)-type Si substrate (figure 2 (a)). The “shelf” corresponds to ~1 eV-wide bandgap with the Fermi level near its low-energy side. Valence and conduction bands are showed with the inclined sections at higher negative and positive voltages, respectively.

For elevated parts of the STM image (presumably carbon clusters), the tunneling spectra were notably different (figure 2 (b)). Their shapes were approximately symmetrical, with continuous DOS and no bandgap, as it can be expected for carbon in the \( sp^2 \)-hybridized state. Illumination of the sample
with optical radiation – for instance, its exposure to the laboratory ambient light – resulted in notable increase of the tunneling I-V curves’ slopes near zero voltage. This effect may reflect delocalization of excited electrons, in good agreement with the previously observed property of photoconductivity [5] inherent in such films.

However, for STM probe positions against some of the clusters, the I-V curves of tunneling current recorded in the dark had unusual shapes (figure 2 (c)), reproduced in many successive voltage sweeps. They had increased noise component and included intervals where signs of \( I \) and \( U \) were opposite. The effect of illumination in this case was very strong – the curves became much more similar to those for film islands of the other type but remained notably displaced with respect to the center of coordinates (figure 2 (d)). We believe that such sites belong to carbon clusters electrically insulated from the rest of the film and from the substrate. The irregular dark-current characteristics result from their electrical charging during the measurements. Optical illumination produces hot electrons, which spoils insulation of such clusters. Simultaneously, it induces photovoltaic effect. Remarkably, that the I-V plot shown in figure 2 (d) crosses the horizontal axis at \( |U| \approx 0.3 \) V, which equals to the photovoltage value determined by the contact method in [5].

Figure 2. Tunneling current/voltage curves (integrated STS spectra) measured for three typical spots at a carbon island film on p+Si substrate (a) Spot 1 chosen in a recession between carbon islands, in comparison with a typical I-V tunneling curve measured for a clean KDB-1 substrate with the oxide layer removed; (b) Spot 2 at one of the islands; the inset shows rescaled and smoothed characteristics near the 0 point. (c) Spot 3 at another carbon island; four I-V curves measured in the dark. (d) I-V curve measured at the same spot 3 with ambient light allowed to fall onto the sample.
4. Conclusion
The performed STM/STS characterization of a carbon film sample capable of low-macroscopic-field electron emission and photosensitivity allowed us to establish or confirm the following experimental facts:

- the film is comprised by clusters of carbon in the state of sp\(^2\) hybridization with lateral dimensions of the order of tens of nm;
- the film is discontinuous and open areas of the substrate are exposed at the surface between the clusters;
- some of the clusters are isolated from the rest of the film and from the substrate, while others are electrically connected with the substrate;
- optical illumination of moderate intensity (ambient light) substantially increases local conductivity of graphitic clusters, presumably producing a long-living population of hot electrons.

The listed facts concerning the properties of smooth-surface carbon cluster films possessing the capability of low-macroscopic-field electron emission are in good agreement with the combined hot-electron/thermoelectric emission mechanism suggested in [14, 16].

Acknowledgments
The authors are grateful to A.V. Arkhipov and V.S. Osipov for cooperation.

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