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Full Length Article

Treatment of surfaces with low-energy electrons

L. Frank[a,*], E. Mikmeková[a,b], M. Lejeune[c]

[a] Institute of Scientific Instruments of the CAS, v.v.i., Královopolská 147, 61264 Brno, Czechia
[b] FEI Company, Achtseweg Noord 5, 5651 GG Eindhoven, The Netherlands
[c] LPMC – Faculte des Sciences d'Amiens, Universite de Picardie Jules Verne, 33 rue Saint Leu, 80039 Amiens Cedex 2, France

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ABSTRACT

Electron-beam-induced deposition of various materials from suitable precursors has represented an established branch of nanotechnology for more than a decade. A specific alternative is carbon deposition on the basis of hydrocarbons as precursors that has been applied to grow various nanostructures including masks for subsequent technological steps. Our area of study was unintentional electron-beam-induced carbon deposition from spontaneously adsorbed hydrocarbon molecules. This process traditionally constitutes a challenge for scanning electron microscopy practice preventing one from performing any true surface studies outside an ultrahigh vacuum and without in-situ cleaning of samples, and also jeopardising other electron-optical devices such as electron beam lithographs. Here we show that when reducing the energy of irradiating electrons sufficiently, the e-beam-induced deposition can be converted to e-beam-induced release causing desorption of hydrocarbons and ultimate cleaning of surfaces in both an ultrahigh and a standard high vacuum. Using series of experiments with graphene samples, we demonstrate fundamental features of e-beam-induced desorption and present results of checks for possible radiation damage using Raman spectroscopy that led to optimisation of the electron energy for damage-free cleaning. The method of preventing carbon contamination described here paves the way for greatly enhanced surface sensitivity of imaging and substantially reduced demands on vacuum systems for nanotechnological applications.

1. Introduction

Power delivered with an electron beam impinging on a solid surface can be concentrated on a spot of even subnanometer size, so when this power is employed for a reaction leaving a progressively growing layer on the surface, we get a tool enabling us to deposit nanodots or to draw nearly arbitrarily nanostructured patterns. This approach has been used for controlled deposition of, for example, Pt-Si films [1], metals such as Ni and Co [2], magnetic nanostructures on a Co basis [3], silicon oxide [4], etc. However, the majority of published studies have dealt with electron-beam-induced deposition (EBID) of carbon from hydrocarbon precursors. These include deposition of nanotips [5] or various nanofigures [6], masking as an intermediate technological step [7,8], engineering of the biocompatibility of hydroxyapatite [9] and the mechanical properties of a mechanical oscillator [10] or seeking an optimum procedure for cutting samples for cross-sectional transmission electron microscopy [11], etc. The relevant literature contains attempts to optimise the deposition process, for example on semiconductor surfaces [12], but there are larger numbers of papers considering the EBID of carbon as an adverse phenomenon. We might mention contamination of the optics of a multi e-beam lithograph with carbon delivered via chemical species outgassed from a resist [13], contamination of nanoparticles preventing their functionalisation with Raman probe molecules and producing unwanted background signals in Surface Enhanced Raman Spectroscopy [14], deterioration of the dopant contrast observed in a scanning electron microscope (SEM) on semiconductor structures [15] or even the growth of nanodots on mirrors in a free-electron laser [16]. By means of Raman spectroscopy and Atomic Force Microscopy, EBID-grown carbon on Si has been identified as amorphous carbon with an estimated crystallite size of 12.5 nm, raised edges of patterns and some texture [17], as corresponds with long time experience of the SEM users.

EBID of carbon from unintentionally adsorbed hydrocarbon molecules has created an unpleasant experience for SEM users throughout the entire history of this instrumental branch. Hydrocarbons were primarily delivered by mineral oils in pumping systems, but even when these oils are not used any more, adsorption of organic molecules from the atmosphere, vacuum grease,

* Corresponding author.
E-mail address: ludek@isibrno.cz (L. Frank).

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rubber gaskets or even finger marks are sufficient to create a problem. Sufficient is even adsorption of hydrocarbons on the sample surface to be loaded in ultrahigh vacuum (UHV) devices with very clean inner surfaces of chambers, metal gaskets and dry pumping. Beginning with the first studies such as Ref. [18] (in which even papers from the 1940s are cited), contamination layers have been examined as regards their thickness and their influencing by electron current density and beam energy, and even by cooling of the specimen or its neighbourhood [19]. Cooling was found to be effective in reducing the contamination rate. As an alternative, an H_2O vapour environment was found causing electron-beam-induced carbon volatilisation, a process competing with film growth and controlled by electron flux, with surface oxidation observed under conditions of very high electron current. Under optimised conditions, surface modification caused by contamination and oxidation was absent [20]. However, it should be noted that specimen cooling is not commonly available in SEMs, and the ESEM (with elevated gas pressure) is also a specific version of the instrument.

2. Material and methods

Previous observations of the EBID of carbon employed electron energies in tens and units of keV. The principle of the cathode lens with the sample biased to a high negative potential [21] enabled us to use any electron energy with consistent quality of images, so we were able to study the problem of the EBID of carbon from spontaneously adsorbed hydrocarbons for energies down to tens and units of eV, namely in an UHV as well as a standard vacuum microscope. As a testing specimen, we chose single-layer graphene (1LG), specifically a commercially available suspended CVD-grown graphene deposited on lacey carbon and copper mesh, imaged with both reflected and transmitted electrons. The thickness of the sample was tested by means of Raman spectroscopy and according to transmissivity measured at tens and units of eV [22]. At ultralow energies, the contrast between sites differing by a single atomic layer of carbon is high enough [22,23] that the development of the contamination layers can be ideally observed. Radiation damage of 1LG can be revealed (with Raman spectroscopy), while removal of any atomic layer from a 1LG sample cannot be overlooked. Before loading into any of microscopes used for the study (in-house built UHV SEM/STEM and XHR SEM of FEI), we annealed the samples for 30–60 min at about 100 °C in order to evaporate molecular water and at least a part of the adsorbed hydrocarbons. Regrettably, we have no possibility of in-situ heating of the sample in the standard vacuum microscope and the same holds true for the UHV microscope when the STEM holder is used.

In addition to free-standing graphene, we have also verified the cleaning effect on other samples (2D crystals of MoS_2, carbon surface spread with tin balls, and others). These experiments are not discussed in detail hereinafter – our aim was to demonstrate the usefulness of the electron stimulated desorption with a case study employing graphene as a sample that is optimum for verification of the desorption on one hand and checking damage on the other hand.

3. Results and discussion

A fundamental finding was that the transmissivity of 1LG for electrons in tens of eV substantially increases during irradiation with electrons at that energy in a dose ranging in tens of mC cm^{-2} with saturation above 250 mC cm^{-2} (Fig. 1a,b). At the same time, the reflectivity of the illuminated area decreases (Fig. 1c) more or less equally on both the transparent and non-transparent parts of the sample. This indicates a backscattered electron (BSE) emission lower from the clean graphene than from adsorbed layers and should not be misinterpreted as EBID-deposited carbon that we also know as a dark pattern. However, here we do not get darker frames of the area created due to the diffusion of hydrocarbons from the vicinity. The above-sample electric field collimates the secondary electron (SE) emission into the central bore of the detector, so the SE escape detection through this bore and we detect solely BSE emitted beyond a certain polar angle off the optical axis and hitting the detector around the bore. These measurements and micrographs were made under UHV conditions. However, a crucial result of this study is that the effect is available even in a standard high vacuum of the order of 10^{-4} Pa. In this case, the processes of deposition and release are competing as we see in Fig. 1d. Between about 30 and 800 eV, the transmissivity substantially increases due to electron-beam-induced release (hereinafter EBIR). Below about 30 eV the effect is negligible, while above 800 eV the EBID of carbon dominates. Curves such as those in Fig. 1d are not fully reproducible and depend on surface and vacuum conditions. Let us note that we have not observed any charging phenomena on irradiated areas irrespective of the final local transmissivity.

Two plots in Fig. 1d were recorded under identical conditions except that the left one was measured with a sample bias of −1 kV and a dose of 1.8 C cm^{-2}, while the right plot was obtained without the use of any sample bias and the electron dose was only 0.1 C cm^{-2}. Obviously, the electric field above the sample influences the EBID/EBIR process. This was confirmed by comparing fields of view irradiated with the same landing energy of electrons but under different sample bias. In Fig. 2a, we see that a negative bias clearly shifts the EBIR/EBID balance in favour of EBID irrespectively of how

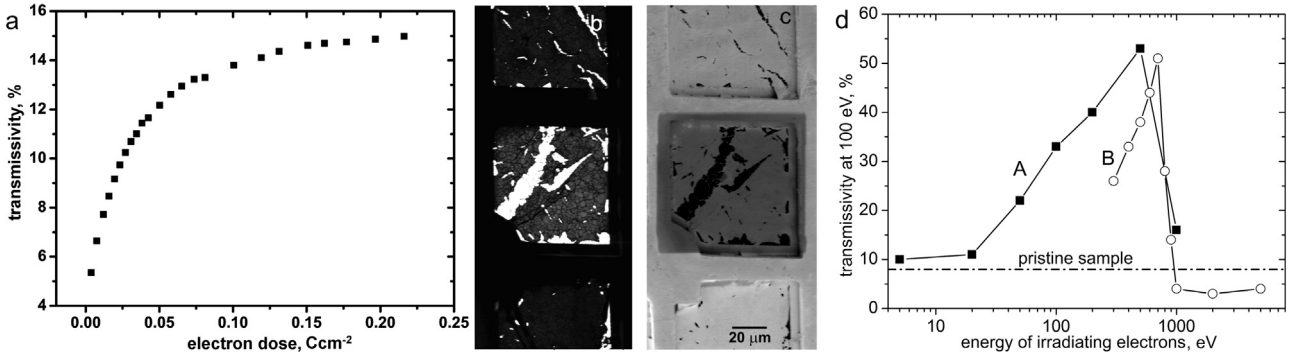

Fig. 1. Development of 1LG due to irradiation with slow electrons.
Suspended CVD-grown graphene deposited on lacey carbon and copper mesh. a, transmissivity of 38 eV electrons in UHV in dependence on their incident dose. b, irradiated field of view shown in transmitted 38 eV electrons in UHV. c, the same micrograph in reflected electrons (scale bar is 20 μm long). d, development of transmissivity of 100 eV electrons through 1LG in a standard vacuum (3×10^{-4} Pa) device in dependence on the energy of electrons irradiating the sample (plot A: sample bias − 1 kV, dose 1.8 C cm^{-2}; plot B: no sample bias, dose 0.1 C cm^{-2}).