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Nanoscale scanning electron microscopy based graphitization in tetrahedral amorphous carbon thin films

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ABSTRACT

Electron beam lithography is a powerful maskless tool to fabricate structures on the nanometer scale. Here, we show that low-keV-electron beams enable a direct patterning of tetrahedral amorphous carbon (ta-C) thin films by inducing a local graphitization without the need for any resist or development process step. Irradiation with 4 keV electrons leads to a local decrease of the ta-C film's electrical resistance and an increase of both the sp^2/sp^3-ratio and the material's work function. We investigate the impact of electron exposure on ta-C by a variety of microscopy as well as spectroscopy methods including scanning tunneling microscope-based current-distance spectroscopy, conductive atomic force microscopy, spatially resolved ultraviolet and x-ray photo emission spectroscopy, and μ-Raman spectroscopy. The electron exposure has been performed under ultrahigh vacuum conditions to prevent from electron-induced deposition of contaminants which may obstruct the application of surface-sensitive analysis techniques to the modified ta-C films.

1. Introduction

Under ambient or vacuum conditions fully or predominantly sp^3-hybridized carbon materials such as diamond and diamond-like materials, e.g., tetrahedral amorphous carbon (ta-C), are in a metastable state. By deposition of energy these materials may undergo a phase change to a graphitic or sp^2-hybridized state. As a consequence thereof, many physical properties including the electrical conductivity, the work function, and the mass density of ta-C change from diamond-like to graphite-like. The electrical conductivity and the work function are expected to increase with the degree of graphitization; the electrical conductivity even over several orders of magnitude [1,2]. The phase change is associated with a reduction of the mass density [3]. Local graphitization of ta-C thin films can be achieved by pulsed laser treatment [2,4], high-energy heavy ion irradiation [5], focused ion beam exposure [6], localized current pulses employing conductive atomic force microscopy (C-AFM) [7], and electron beam exposure with electron energies in the low eV range [8–10] or between 100 keV and several MeV [11–13]. Considering carbon thin films, the reduction of the mass density caused by graphitization leads to an increase of the film thickness or, in case of local graphitization, a local surface swelling [5,14].

In this work we show the possibility of local ta-C graphitization with electron beams in the intermediate energy regime of a few keV, which is commonly used in a scanning electron microscope (SEM) and in common electron beam lithography. To the authors' knowledge this has not been reported yet. Nevertheless, it has been shown that electron irradiation in the same energy range can effect hydrogenated amorphous-carbon (a-C:H), which is a related form of carbon, as long as C-H bonds are present [15]. Furthermore, it can introduce disorder in graphene [16]. Here, we fill the gap of knowledge regarding keV electron induced modification of ta-C, which should be considered when employing electron beam based methods like Auger electron spectroscopy or high resolution SEM imaging. In addition, a possible approach towards applications might be related to the different plasma etching rates of graphitized

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and virgin ta-C [17]. SEMs usually work in a high vacuum of about 10^{-7} mbar where one still has to deal with the deposition of amorphous materials from cracked residual gas and adsorbed molecules. We avoid this contamination by electron exposure in an ultra high vacuum (UHV) and preceding sample annealing without UHV interruption.

2. Experiment

Our ta-C thin films were deposited on p-doped silicon wafers with a resistivity of 0.01–0.02 Ωcm covered by a natural oxide layer using the filtered cathodic vacuum arc method [18,19] at the Dresden-based Fraunhofer Institute for Material and Beam Technology IWS. All experiments described below were performed using a ≈20 nm thick ta-C film with a sp^3-content of ≈73% determined on the basis of a C 1s XPS measurement.

On top of the ta-C films a 12 nm thick Ti marker structure was deposited by molecular beam epitaxy. The Ti patterning has been done by simply using transmission electron microscopy grids as contact masks.

The 4 keV electron irradiation experiments have been performed using an UHV Zeiss Gemini SEM [20] and an Omicron UHV system with integrated SEM-scanning tunneling microscope (STM) combination. The latter allows for electron irradiation followed by scanning tunneling spectroscopy (STS) examination without breaking the vacuum conditions at a base pressure of less than 3×10^{-10} mbar. Our STM tips are based on Pt/Ir wires, which were prepared by cutting and pulling off the wire.

Prior to the electron-beam exposure the samples were heated to 400 °C for approximately 12 h in UHV (Omicron system) or to 130 °C for approximately 9 h (Zeiss Gemini system) in UHV. At 400 °C changes in electrical conduction start to appear, but thermal graphitization is negligible [1,11]. The annealing procedure removes adsorbed molecules, which are thought to be the major source for the deposition of undesired contamination layers during electron exposure.

For the e-beam exposure with the Zeiss Gemini system, a Raith Elphy Quantum lithography system was connected. Square shaped ta-C film areas (edge length: 256 nm) were irradiated with a focussed 4 keV 5.25 nA electron beam in a single-pass meander scan using a step size of 3 nm. The fluence of the electron irradiation has been varied between 0.22 μCμm^{-2} and 6.64 μCμm^{-2}.

The Omicron system has been used to irradiate a micron-sized spot for 16 h with an electron energy of 4 keV and a total charge deposition of 232 μC corresponding to a fluence of approximately 1 μCμm^{-2}. Afterwards current-distance (I(z)) curves were measured at several locations starting on virgin ta-C some micrometers away from the irradiated area, next at the center of the spot, and again on virgin ta-C several micrometers away in another direction. The spot was visible in the SEM image, ensuring an appropriate positioning of the STM tip. The lower secondary electron-yield might be a first indication for a higher work function. Tunneling conditions for suitable STM imaging were achieved with an applied voltage of $V_0 = 3.5$ V and a current setpoint of $I_0 = 30$ pA. At each location, 256 spectroscopic I(z) curves were measured. Subsequently the median of the current data has been calculated.

Assuming a metallic sample and a small gap voltage, the tunneling current in STM measurements depends exponentially on the tip-sample separation. In our case it is necessary to consider the high resistance of the ta-C thin film R_{carbon} when analysing the spectroscopic I(z)-data. We fit this additional resistance in series with the tunneling gap resistance R_{gap}, so that the applied voltage is divided between these two resistances:

$$I(z) = \frac{V_0}{R_{carbon} + R_{gap}} = \frac{V_0}{R_{carbon} + C \cdot \exp\left(2z\sqrt{2m_e\overline{\Phi}}\Big/\hbar\right)} \quad (1)$$

V_0 is the applied voltage between tip and sample contact. R_{gap} is calculated from a fit constant C, the tip sample separation z, the electron mass m_e and the average tunnel barrier height $\overline{\Phi}$. $\hbar$ denotes the reduced Planck constant. One should keep in mind that this model neglects any voltage dependency of both R_{carbon} and R_{gap}. Strictly speaking, true Ohmic behavior is neither expected for the hopping conductivity in ta-C [21], nor for the voltage-dependent tunneling barrier in the intermediate voltage range [22]. Nevertheless, equation (1) is a useful basic approximation to evaluate I(z) spectroscopy data of low conductivity materials like ta-C.

Topography and local conductivity measurements have been performed in ambient conditions using a Digital Instruments Dimension™3100 scanning probe microscope. To resolve a possible surface swelling of the graphitized area due to the reduced mass density tapping mode AFM scans have been taken. C-AFM, or spreading resistance imaging, has been done by contact mode scans with Pt/Ir-coated cantilevers that allowed for local conductivity measurements.

Laterally resolved photoemission spectroscopy measurements have been performed with a NanoESCA, which was designed by Omicron Nanotechnology and combines the advantages of photoemission electron microscopy (PEEM) and ultraviolet/X-ray photoemission spectroscopy (UPS/XPS). Here, the two-dimensional electron image of the sample surface is generated and energy filtered by a PEEM column and an aberration corrected double hemispherical energy analyzer [23,24]. The instrument is equipped with a He discharge lamp and a focused monochromatized Al K_α source providing photons with energies of 21.2 eV for UPS and 1486.8 eV for XPS, respectively. The C 1s core level XPS spectra were recorded with an energy resolution of about 0.4 eV. To determine the sp^2/sp^3-ratio these spectra are fitted by two Voigt profiles corresponding to sp^2- and sp^3-hybridized carbon. The work function Φ is related to the secondary electron cutoff in UPS and can be determined with an accuracy better than 0.1 eV. The measured area was restricted to a circle, 17 μm in diameter, by the iris and a circular micro aperture that was positioned in the first intermediate image plane. Spectra taken on the electron-irradiated region are compared to those of the virgin ta-C film several micrometers away from the irradiated spot.

3. Results and discussion

Fig. 1 shows a spatially resolved current map of ta-C containing four square-shaped areas of $(256\ nm)^2$ that were exposed to 4 keV

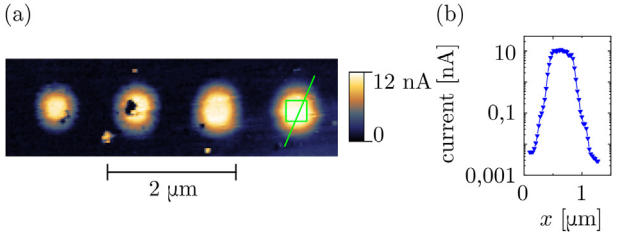

Fig. 1. (a) C-AFM image of ta-C showing four areas after 4 keV electron irradiation. The green square indicates the irradiated area. Fluence (from left): 0.22; 0.66; 1.55; 2.21 μCμm^{-2}. Sample bias during C-AFM mapping: 5 V. Please note the logarithmic color scale. The black spot in the second irradiated area is caused by a non-conductive particle. (b) Line section through the C-AFM map shown in (a). (A colour version of this figure can be viewed online.)