



Graphite oxide Auger-electron diagnostics



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ABSTRACT

Graphite oxide (GO) nanofilms on the SiO₂/Si surface have been studied by photoelectron spectroscopy (XPS) with synchrotron radiation and by Auger electron spectroscopy (AES). Auger electron energies were determined for the basic functional GO groups: hydroxyl (C–OH) and epoxide (C–O–C). The data obtained enabled developing a technique for the GO chemical and elemental composition determination. The technique allows controlling the hydrogen content in GO despite the impossibility of Auger emission from hydrogen.

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1. Introduction

Graphite oxide (GO) is of great interest because of its unique physical–chemical properties [1–5]. GO flakes created by oxidative exfoliation of graphite form a colloidal water suspension that, being evaporated, leaves a GO film almost on any surface [1–3]. Thermal reduction enables variation of the GO bandgap width within a wide range to control GO optical characteristics and conductivity [6,7]. These properties make the GO submicron films a promising material for fabricating transparent conducting films and flexible displays [1,3,4], supercapacitors, and accumulators [5]. Reduction of monolayer GO films is used for graphene fabrication [1,3]. The GO properties are governed by its chemical composition that drastically depends on peculiarities of the GO fabrication and modification techniques. Thus the evolvement of GO chemical composition diagnostics is one of the topical tasks of the GO research and development. One of the most efficient and advanced methods for the GO composition analysis is X-ray photoelectron spectroscopy (XPS), especially that with using synchrotron radiation. It has been established by this method that GO contains mainly the carboxyl (CO–OH), epoxide (C–O–C) and hydroxyl (C–OH)

functional groups surrounding GO flakes and being bound to their surfaces [1,4,6,8–12]. The essentially low-cost Auger electron spectroscopy (AES) is not at present used in the GO chemical analysis, though examples of studying GO Auger spectra are known [13,14], as well as of revealing with AES fine chemical variations in the carbon material structures [15]. Extended and complicated Auger line shapes prevent using AES for chemical analysis. Additional difficulties may arise due to the electron-beam-induced static charging of the sample, which may be especially intense in the case of practically important relatively thick GO films in the nanometer and submicron thickness range. In this work, an Auger-technique has been developed for the chemical composition analysis of dielectric GO films being under static charging.

2. Experimental

The graphite oxide was synthesized via oxidation of the natural crystalline graphite by potassium permanganate in sulfuric acid in the presence of sodium nitrite as in Ref. [6,16,17]. Relatively thick GO films were fabricated on silicon substrates by evaporating a concentrated drop of the GO colloidal solution (6%). The film morphology and thickness were studied by scanning electron microscope (SEM) JEOL JSM-7001F (JEOL). The XPS investigation of the chemical composition and electronic structure was performed by using a photoelectron spectrometer equipped with a SPECS

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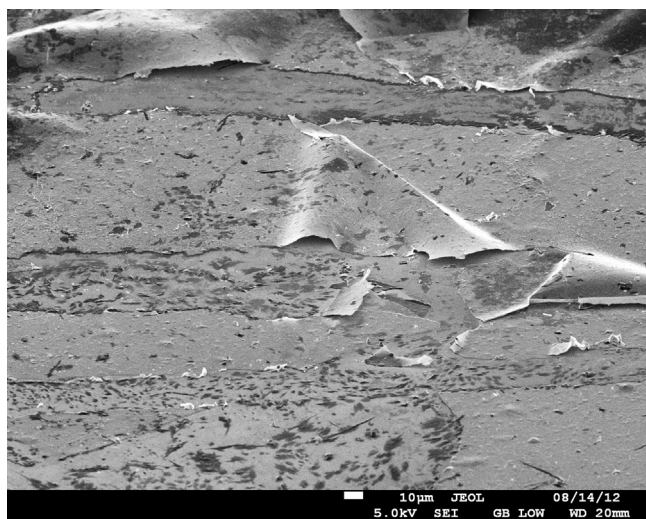


Fig. 1. SEM-image of a sample area with horizontal size $l = 280 \mu\text{m}$.

hemispherical analyzer at the Russian–German synchrotron radiation beamline of the BESSY-II electron storage ring (Berlin) [18]. The total XPS spectral resolution was $\Delta E = 0.15 \text{ eV}$. The same objects were studied also by AES with the LHS-11 (Leybold-AG) electron spectrometer. Auger electrons were excited by primary electrons with energy $E_0 = 1500 \text{ eV}$ and detected in the counting mode with a constant relative energy resolution ($\Delta E/E = \text{const}$). The Auger electron spectra were measured relative to the Fermi level. Therefore, to reduce the energies given below to the vacuum level, one should subtract the spectrometer work function $e\phi = 4.7 \text{ eV}$ that was measured using the $\text{Au}4f_{7/2}$ gold photoelectron line as a reference. Basic vacuum in both spectrometers was $P \sim 2 \times 10^{-10} \text{ Torr}$. Sample surfaces were cleaned from atmospheric adsorbates by long-term keeping in high vacuum, which was shown for thermally reduced GO films to be almost as efficient as vacuum heating at the temperature of $\sim 400^\circ\text{C}$ [6]. Films for both experiments were prepared from one and the same solution in one and the same way.

3. Results and discussion

Fig. 1 presents the SEM-image of a surface area of one of the films under study. It is clearly seen that the surface consists of unusually large sheets (flakes) whose characteristic dimensions amount up to hundreds of microns. Analysis of the SEM images of the sheet edges showed that their thickness does not exceed 20 nm. The inter-sheet gaps (scratches) visible in the image are overlapped by thinner flakes, which is evidenced by traces of the $\text{Si}2p$ silicon substrate contribution to the photoelectron wide scan survey spectrum measured at photon energy $h\nu = 701.0 \text{ eV}$.

Photoelectron spectra of the carbon $\text{C}1s$ core shell presented in Fig. 2 were measured for two sample areas containing mainly either “thick” or “thin” GO flakes. Dimensions of these areas were determined by the photon beam cross-section ($\sim 0.2 \times 1 \text{ mm}$). The “thick” film spectrum exhibits peaks corresponding to three known GO functional groups: hydroxyl C-OH ($E_B = 286.1 \text{ eV}$), epoxide C-O-C ($E_B = 288.4 \text{ eV}$) and carboxyl O=C-OH ($E_B = 290.4 \text{ eV}$). The respective binding energies (E_B) of the $\text{C}1s$ core electron are close to those obtained earlier in Ref. [1,8–11], though the differences amount up to 0.2–0.5 eV. The GO spectrum contains almost no graphite sp^2 state contribution (C=C). This confirms high efficacy of the oxidation technique used. Note that the most intense hydroxyl line of the “thick” film spectrum is shifted toward higher binding energies by $\sim 0.2 \text{ eV}$ as compared with the respective line of the “thin” film and the line of the graphene oxide film studied in our previous work [6].

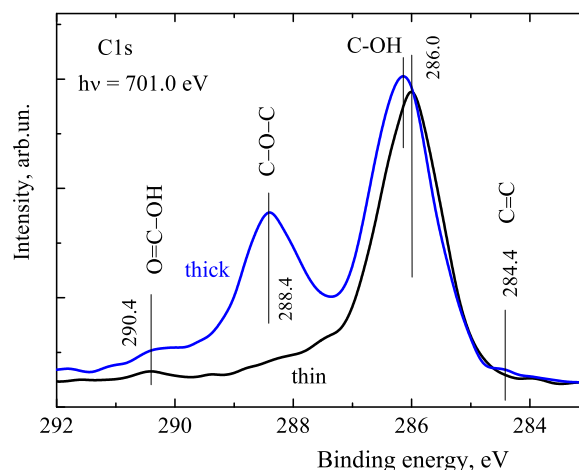


Fig. 2. $\text{C}1s$ photoelectron spectra of the “thick” and “thin” GO films. The photon energy was $h\nu = 701 \text{ eV}$.

This shift is probably caused by low photon-beam-induced static charging of the “thick” GO film. As in the graphene oxide films studied earlier [6], contributions of the carboxyl (CO-OH) group and, especially, of the epoxide (C-O-C) group proved to be significantly less than those in the GO spectra in Ref. [8–11]. This is probably due to large sheet-flake sizes in our samples and, hence, to low contributions of the carboxyl and, partly, epoxide groups that tend to localize at the flake edges [1].

To develop Auger diagnostics of the GO chemical composition, it is necessary to determine the CKVV Auger transition energies in the main functional groups. In other words, it is necessary to find the energy position of the differential spectrum (dN/dE) minimum located at the relatively sharp edge of the wide and intricate initial spectrum $N(E)$ (Fig. 3). Fig. 3a presents the differential CKVV Auger spectra obtained by irradiating the GO film under study with X-ray photons ($h\nu = 701 \text{ eV}$) and electrons ($E_0 = 1500 \text{ eV}$). The Auger spectrum of the X-ray experiment contains some contribution of the analogous data on the graphene oxide film collected in our previous research [6]. Adding the additional data enhanced the spectrum statistics. Since the film was charged by the diagnostic electron beam to $\Delta E_e \sim 1 \text{ eV}$, the AES electron spectrum was corrected, namely, it was shifted toward lower energies so that its features coincided with those of the photo-induced spectrum. Both spectra exhibit features that we have identified as the dominating contribution of the hydroxyl group at $E_{\text{CKVV}}(\text{C-OH}) = 268.0 \text{ eV}$, additional contribution of the epoxide group at $E_{\text{CKVV}}(\text{C-O-C}) = 271.5 \text{ eV}$, and insignificant contribution (276.2 eV) of two possible phases of carboxyl (CO-OH) and graphite (C=C) (Table 1). The estimation errors of these energies did not exceed $\varepsilon = \pm 0.5 \text{ eV}$.

Identification of the energy positions sequence for the main phases (epoxide and hydroxyl) was based on the analysis of the X-ray Auger spectrum for the “thin” film practically containing only hydroxyl contribution and for the “thick film–thin film” difference spectrum exhibiting only the epoxide group contribution (Fig. 2). These spectra are characterized by poorer statistics, but each contains almost exclusively the contribution of only one known functional group. These spectra gave additional estimates of the Auger transitions energies in the hydroxyl ($\sim 268.5 \text{ eV}$) and epoxide ($\sim 271.2 \text{ eV}$) groups. The estimates proved to be very close to the corresponding energies obtained above with higher accuracy (Table 1) and enhanced the reliability of our identification.

Earlier the photo-induced Auger spectra of GO films were measured in Refs. [13,14]. The hydroxyl group dominated in both studies. The problem of the spectra decomposition into constituents corresponding to different phases was not stated in

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