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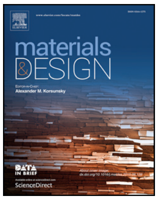

Thermally induced modification of the graphene oxide film on the tantalum surface

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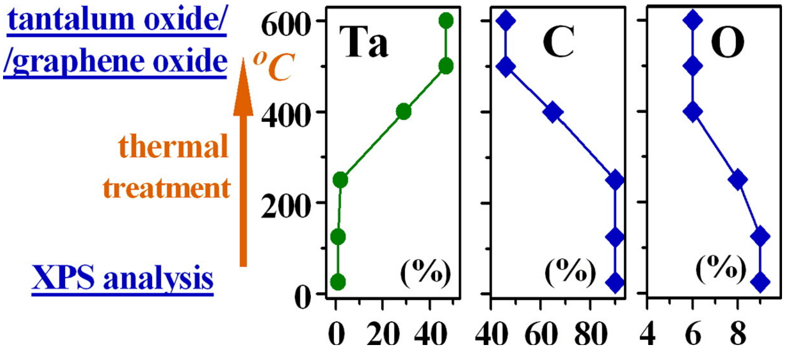
HIGHLIGHTS

- The *ex situ* deposited graphene oxide thick film on the polycrystalline Ta surface demonstrated porosity about 1%.
- The thermal annealing of the graphene oxide in ultra high vacuum was followed by an increase of the uncovered Ta surface.
- The formation of the TaC compound on the Ta surface in presence of graphene oxide at elevated temperatures was determined.
- The concentration of the phenolic component within the graphene oxide layer was stable after the annealing at 400 °C.

GRAPHICAL ABSTRACT



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ABSTRACT

The interface chemical reactions, the deoxygenation and the overall thermal stability of the *ex situ* deposited graphene oxide (GO) thick film on the polycrystalline tantalum surface were studied by means of x-ray photoelectron spectroscopy (XPS) at room temperature and after annealing up to 600 °C. The evolution of the Ta_{4f}, C_{1s} and O_{1s} XPS core level spectra from the Ta/GO structure under study upon the increase of the annealing temperature was investigated with the reference to the uncovered Ta substrate surface. In the Ta/GO structure the Ta relative atomic concentration was about 1% at room temperature due to the low porosity of the GO layer while the thermal desorption of the overlayer at the elevated temperatures was accompanied by an increase of the Ta concentration up to 47% at 500 °C. The C atoms relative concentration started decreasing after the annealing at 250 °C accompanying the thermal desorption of the GO overlayer. The formation of the TaC compound starting from the 250 °C annealing temperatures was determined. The relative oxygen concentration in the GO thick film was decreased upon increasing the annealing temperature accompanying both the thermal desorption of the GO material and the thermal reduction of the GO film.

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1. Introduction

Electronic and thermal properties of thin film structures made from graphene oxide (GO) and reduced graphene oxide (rGO) attract large scientific interest due to promising device applications [1–6]. The reduction of GO can be made using chemical, electrochemical and thermal approaches in air and in ultrahigh vacuum (UHV) conditions [7,8]. The effect of the deposition temperature and of the annealing treatment on the structural and the electronic properties of metal oxide and of graphene oxide materials was addressed intensively during the last years [9–14]. The thermal assisted synthesis was reported to be efficient for the preparation of the GO films and of the hybrid nanocomposites containing GO [13–17]. The covalent bonding between the components of the hybrids, such as C-O-Zn bonding in GO/ZnO composites, was determined using the electron spectroscopy techniques [13,16]. The possible applications of the hybrid nanocomposites containing GO and rGO in photoelectric, photoluminescence and gas-sensing devices was pointed out by a number of research groups [6,13–16]. The oxygen contents in rGO, which reflects the degree of reduction can vary depending on the preparation approach and the set of conditions chosen for the reduction procedure, and the x-ray photoelectron spectroscopy (XPS) studies have contributed largely to characterization of rGO composition [7,8,18,19]. Moreover, the relative concentration of the hydroxylic, carboxylic, carbonylic, epoxy and other oxygen containing groups in rGO (Fig.1) may differ depending on the deoxygenation procedure used because of the different degree of the stability of those oxygen containing groups in rGO [18–20]. An advantage of the thermal reduction of GO is that it allows removal of selected oxygen-containing groups by choosing different annealing conditions [1,18,20]. Particularly, changing the annealing temperature within the 100 °C–1000 °C range one can remove either electron-donating or electron-withdrawing oxygen-containing groups and, as a result, obtain the rGO material demonstrating either electron type or hole-type of conductivity [1]. There has been reported that deposition of GO from a suspension onto solid surfaces would provide the possibility of tuning the interface electronic properties such as the underlayer electronic work function, the height of the potential barrier at the interface [7,21]. Such interface modification in planar structures as well as in bulk composites might lead to improvement of electric, photovoltaic and switching device parameters [3–5,21,22,23]. Formation of GO and rGO composites with conjugated organic materials, metal oxides and metals is accompanied by electronic charge transfer and possible covalent bond formation [5,6,24–26]. In this paper we present the XPS results characterizing the overall stability, the deoxygenation and the interface interaction of graphene oxide thick film on the tantalum surface upon the thermal treatment at elevated temperatures.

2. Experimental

The graphene oxide (GO) powder was purchased from Akkolab (Russia) and used as received. The manufacturer data reported the lateral flake size within 200–1500 nm, maximum 10 atomic layers forming a flake and the average oxygen contents above 10%. The powder was dispersed in toluene and subjected to ultrasonic treatment for 10 min by using the ultrasonic homogenizer (Bandelin Sonopuls HD 2070, f ~ 20 kHz). Though it is known that GO dispersion in non-polar aromatic solvents is not as stable as in alcohol solvents, we chose toluene because of its use for dissolving conjugated organic molecules. So the results on the dispersion made this way may readily be used in preparing liquid phase precursors for composite materials made from GO and conjugated organic molecules [6,22]. The GO films were drop cast onto the substrate surface within a few seconds after stopping the ultrasonic treatment to ensure the homogeneity of the suspension during the deposition. The average film thickness was estimated to be 500 nm, based on the dispersion concentration, the drop cast volume and the sample surface area. The polycrystalline tantalum (Ta) foil annealed (Goodfellow Cambridge Ltd.) was cleaned in organic solvents and baked for 1 h at 100 °C to ensure the solvent evaporation. Ta is a practical substrate material due to its high melting point values. However, one should expect the presence of the tantalum oxide on the surface because even during the thermal surface cleaning the oxygen diffusion from bulk may occur [27,28]. After the film preparation in air the film and the reference sample of the Ta substrate without the film overlayer were placed into the UHV conditions and subjected to the x-ray photoelectron spectroscopy (XPS) studies. The XPS measurements were performed using the Escalab 250Xi instrument (Thermo Fisher Scientific Inc.) equipped with the Al Kα (1486.6 eV) excitation source. The element core level spectra were recorded in the 20 eV constant pass energy mode, using the XPS spot size of 650 μm. The energy resolution of the experiment was about 0.3 eV. The base pressure was kept below 10^{-7} Pa during the XPS experiments, in the case of use of electron-ion compensation system Ar partial pressure was kept below 10^{-5} Pa. The instrument was equipped with a standard sample holder for heating the sample up to 900 °C. The library of the reference XPS spectra including the atomic registration sensitivity factors was provided by the instrument manufacturer within the Avantage Data System for XPS, as well as the other XPS data collection [29] were used for the analysis. The peak deconvolution was made using the Avantage software (Thermo Fisher Scientific Inc.) which was set to a Shirley background subtraction followed by peak fitting to Voigt functions having 80% Gaussian and 20% Lorentzian character. The surface structure of the Ta substrate and the GO film under study was examined using the atomic force microscopy (AFM) technique. The contact mode AFM measurements were performed using the Integra Spectra instrument (Spectrum Instruments Ltd.).

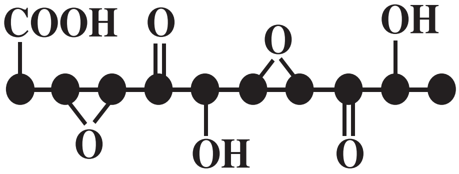

Fig. 1. A schematic side view of a graphene oxide (GO) layer fragment illustrating carbon atoms in the graphene basal plane depicted as solid circles and the typical oxygen-containing functional groups attached to the carbon layer.

3. Results and discussion

The atomic composition analysis of an *ex situ* prepared GO film on the Ta surface should consider the contribution of the carbon-containing and oxygen-containing surface adsorbates as well as of the tantalum oxide into the resulting XPS spectra measured. It was therefore necessary to characterize the relevant XPS core level maxima measured from the Ta substrate without the GO film overlayer. The Ta_{4f}, C_{1s} and O_{1s} core level spectra measured at room temperature and after annealing at elevated temperatures are shown in Fig. 2. The annealing was conducted for 30 min at each of the temperatures chosen. The annealing of the Ta substrate at 250 °C did not change the Ta_{4f}, C_{1s} and O_{1s} core level peak structure or relative intensity compared to the case of the room temperature (25 °C) (Fig. 2a). The Ta_{4f} core level spectrum demonstrates the double peak at 27 eV ($Ta4f_{7/2}$) and 29 eV ($Ta4f_{5/2}$) corresponding to tantalum pentoxide and by the double peak of lower intensity at 22 eV ($Ta4f_{7/2}$) and 24 eV ($Ta4f_{5/2}$) typical for metallic Ta [28,30]. The C_{1s} core level spectrum at room temperature and after the annealing at 250 °C (Fig. 2b) is situated at 285.5–285.0 eV binding energy which is indicative of the presence of the surface-adsorbed carbon impurities [29]. The O_{1s} core level spectrum without annealing and after the annealing at 250 °C (Fig. 2c) is situated at 531 eV approximately. The major contribution to this peak is provided by the tantalum pentoxide [30], which corresponds well to the observation of the Ta^{5+} oxidation state in the Ta_{4f} peak profile (Fig. 2a). The relative atomic