

Graphene on quartz modified with rhenium oxide as a semitransparent electrode for organic electronics

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Abstract

The presented research shows that commercially available graphene on quartz modified with rhenium oxide meets the requirements for its use as a conductive and transparent anode in optoelectronic devices. The cluster growth of rhenium oxide enables an increase in the work function of graphene by 1.3 eV up to 5.2 eV, which guarantees an appropriate adjustment to the energy levels of organic semiconductors used in organic light-emitting diode devices.

1. Introduction

The displays of many common devices such as TV sets, mobile phones, and cameras are built on organic light-emitting diodes (OLEDs) due to the unrivalled image quality resulting from accurate colour reproduction. The amazing and very rapid progress in the development of the OLEDs manufacturing technology makes it widely regarded as the technology of the future [1]. One of the most important elements in the construction of an OLED is a highly conductive and transparent electrode. Currently, in a typical OLEDs design, an electrode is made of an indium tin oxide (ITO) layer deposited on glass. Despite its many advantages, the ITO layer has a very serious disadvantage of brittleness. This makes the construction of flexible displays with ITO layer highly challenging. Therefore, at present, there is an intense search for alternative materials

that can be used as flexible electrodes in OLEDs and photovoltaic cells [2].

It is well known that graphene conducts electricity and heat very well, is transparent in the visible range of electromagnetic radiation, and is also highly flexible. All the above characteristics make it a great candidate as a potential conductive and transparent electrode in optoelectronic devices such as OLEDs and photovoltaic cells. However, graphene in its undoped form is characterized by a too low work function (3.9–4.5 eV), which makes it impossible to adjust the energy levels of organic semiconductors used to make the optoelectronic devices [3, 4]. One of the methods of adjusting the energy levels of graphene is applying a transition metal oxide layer [5–7], resulting in a hybrid system with desired properties. An excellent example of this approach is the work of Meyer *et al.* [6], in which they showed an OLED with an anode based on a trilayer graphene deposited on glass, which was modified with a thin (5-nm) layer of molybdenum oxide (MoO₃). It

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was recently showed by the authors that the same effect can be obtained by using a thinner layer of crystalline molybdenum oxide [8–11]. The authors have also made attempts to modify the work function of graphene using other transition metal oxides such as rhenium oxide [5] and titanium oxide [12]. The authors' original approach to obtain a transition metal oxide layer is first to optimize the process of fabricating an appropriate layer on the surface of a highly oriented pyrolytic graphite (HOPG), which is similar to graphene. In the next step, an analogous growth is carried out on graphene as shown in the works [8, 9].

During the research, the authors were able to fabricate a fully functional OLED with a graphene electrode. For this purpose, they were the first in the world to use bilayer graphene, which was epitaxially fabricated on a surface of a silicon carbide crystal SiC(0001) using the chemical vapour deposition (CVD) method (ITME, Poland). Rhenium oxide was used to increase the work function of bilayer graphene [5]. It was demonstrated that such a hybrid system worked in OLEDs as a conductive and transparent anode. However, due to the very high cost of bilayer graphene on SiC, they were not able to fully optimize the structure and fabrication processes of OLEDs. Therefore, it was decided to use for further research an approximately 10 times cheaper equivalent – graphene on quartz, which is commercially offered by MSE Supplies LLC (USA), in which graphene is prepared on a copper foil by the CVD method and then transferred onto quartz using polymer: poly(methylmethacrylate) (PMMA) in a wet transfer process.

The manufacturer guarantees the sheet resistance of the tested graphene on quartz at a very low level of only $360 \pm 30 \Omega/\square$, a value lower than the sheet resistance of graphene on SiC ($> 600 \Omega/\square$) [13].

It is worth noting that 2D materials, such as graphene and graphene oxide, can be used in optoelectronic devices not only as a conductive electrode, but also as a hole-injection layer, blocking or transport layer. For example, graphene oxide on ITO can be used as a hole-injection layer in OLEDs which leads to a reduction of the device threshold voltage to a value of 3.0 V, which is lower than the commonly used polymeric layer of a mixture of two PEDOT:PSS ionomers (3.3 V) [14].

In this paper, the results of the authors' study on the modification of the graphene work function with the use of thermally deposited rhenium oxide under ultrahigh vacuum conditions (pressure of $\sim 6 \times 10^{-9}$ mbar) are presented. The studies show that a relatively low-cost graphene on quartz modified with rhenium oxide meets all the basic requirements that are set for a transparent anode and can be successfully used in place of a much more expensive bilayer graphene on SiC(0001).

2. Results

Figure 1(a) shows the topographic image of graphene on quartz obtained using an atomic force microscope (AFM). The Ntegra Aura AFM microscope (NT-MTD) operating in semi-contact mode under ambient conditions was used. The authors' AFM study shows that the graphene layer coverage is better than 95%, and it is continuous with marginal defects and polymer contaminations. The graphene

is covered with small amount of contaminations (PMMA polymer residues) observed as bright features, which persisted on graphene after a dissolution of a polymer layer acting as the supporting layer in the wet transfer process [15, 16]. Additionally, some typical graphene defects such as dark cracks and bright wrinkles can be seen in Fig. 1(a). The presence of wrinkles and cracks can be explained in terms of the mechanical handling of graphene during its transfer to the substrate and by the presence of wrinkles in the as-grown graphene on the copper foil [16]. The crystallinity and roughness of a Cu substrate is one of the most important factors that influence the formation of wrinkles and cracks in as-grown graphene during cooling in the CVD process [17]. Note that a minimum critical length is necessary to wrinkle the graphene layer and stabilise the wrinkles. Graphene wrinkles with lengths smaller than the critical value are not stable and can be removed by thermal annealing [18]. Atomic defects existing on a graphene film were not seen using the AFM, due to a limited resolution. Figure 1(b) shows an AFM image of rhenium oxide, with a thickness of 10 nm, deposited on graphene by a thermal deposition from a crucible filled with Re_2O_7 powder under ultrahigh vacuum. The thickness of the rhenium oxide layer was estimated using a quartz microbalance. Here, the thickness refers to a hypothetical uniform single-crystalline multi-layer of Re_2O_7 grown on the substrate. The authors' AFM study shows that the growth of a compound with the Re_2O_7 formula on graphene is cluster-like. This indicates that the free diffusion path of arriving compounds is very short due to the possible existence of atomic defects in graphene structure. Presumably, these defects are working as pin sites immobilizing diffusing rhenium oxide clusters. This combined with the relatively strong rhenium oxide/rhenium oxide interaction leads to the growth of separated clusters according to the Volmer-Weber (VW) model [19]. This explains why atomically flat crystalline layers of rhenium oxide on graphene could not be obtained in the authors' study despite great experimental efforts. Moreover, for small coverages, a high mobility of rhenium oxide clusters on graphene was observed, which made the correct AFM imaging difficult, but which supports the hypothesis of the VW model. It also shows that the binding of the clusters to the pin sites is relatively weak allowing for their manipulation using the AFM. The study shows that the growth of rhenium oxide on graphene deposited on quartz is similar to the growth of rhenium oxide on graphene obtained on SiC(0001) [5].

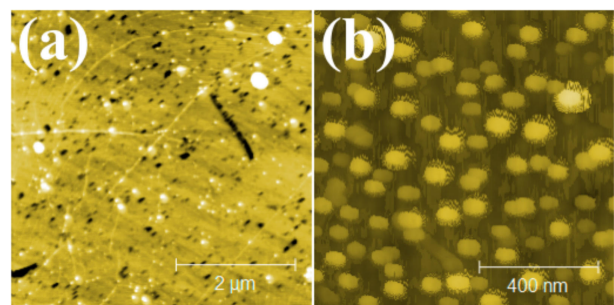


Fig. 1. AFM topographic images of graphene on quartz transferred from copper (a), rhenium oxide with a thickness corresponding to a 10 nm layer deposited on the surface of a graphene/quartz system (b).

To qualitatively analyse the chemical composition of the clusters formed on graphene, X-ray photoelectron spectroscopy (XPS) studies were performed. Figure 2(a) shows the XPS results in the electron binding energy region of the 4f core states for rhenium with a thickness corresponding to a 10 nm layer. It should be noted that graphene was annealed at 325 °C before rhenium oxide deposition to remove PMMA polymer residues. A Phoibos 150 hemispherical electron energy analyser (SPECS) with a 2D-CCD detector was used in this study. The sample was exposed to radiation from a DAR 400 lamp operating with a Mg K α electrode at an energy of 1253.64 eV. CasaXPS software was used to perform the deconvolution of the individual spectral lines. The analysis of the spectra began by removing the background using the Shirley method. A Gauss-Lorentz product function fit [GL(75)] was then performed with a full width at half maximum (FWHM) for all lines of 1.7 eV. Due to the spin-orbit coupling, the occurrence of a characteristic 4f_{7/2}–4f_{5/2} doublet with an energy splitting of 2.4 eV with an integral intensity of 4:3 was considered in the analysis of the Re 4f spectrum. The XPS spectra show the occurrence of two different rhenium oxide phases. Mainly, the Re₂O₇ phase is observed with the characteristic 4f_{7/2}–4f_{5/2} doublet with energies of 45.3 eV and 47.7 eV, respectively, which is comparable with literature data [20]. In addition, a ReO₃ phase with a characteristic 4f_{7/2}–4f_{5/2} doublet in small amounts with energies of 42.9 eV and 45.3 eV was observed, respectively. Since ReO₃ exhibit a metallic conductivity similar to that of copper, a local conductivity enhancement is expected. Similar results were also obtained for rhenium oxide with different thicknesses, which was deposited onto graphene on SiC(0001) by thermal deposition from a crucible filled with ReO₃ powder under ultrahigh vacuum conditions, where an increase in the Re₂O₇ phase was also observed [5].

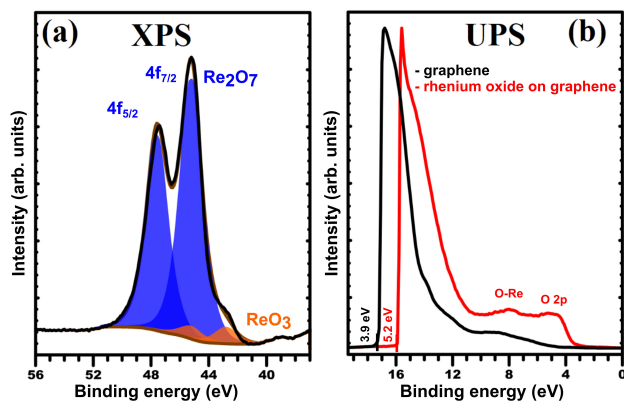


Fig. 2. XPS studies of graphene modified with rhenium oxide of a thickness corresponding to a 10 nm layer in the electron binding energy region of the core 4f states for rhenium (a). UPS studies over a wide energy range for pure graphene and for modified graphene with rhenium oxide of a thickness corresponding to a 10 nm layer (b).

To determine the work function of graphene modified with rhenium oxide, ultraviolet photoelectron spectroscopy (UPS) studies were performed. Figure 2(b) shows UPS studies for pure graphene annealed at 325 °C and for annealed graphene modified with rhenium oxide with a thickness corresponding to a 10 nm layer. For the study,

a He α line with an energy of 21.23 eV using a HIS-13 UV lamp was used. To correctly measure the backscattered electron emission edge, a negative potential of 3.1 V was applied to the sample. Calibration of the UPS results was done by determining the Fermi level for the pure Au(111) surface. The black curve in Fig. 2(b) shows the UPS results collected for pure graphene. The work function estimated by determining the backscattered electron emission edge for pure graphene on quartz is 3.9 eV. This value is smaller than the work function obtained in our previous study for bilayer graphene on SiC(0001), which was 4.19 eV [5]. On the other hand, the red curve in Fig. 2(b) shows the UPS results for graphene modified with rhenium oxide of a thickness corresponding to a 10 nm layer. The work function estimated for the modified graphene is 5.2 eV. The observed very large increase in the value of work function for modified graphene by +1.3 eV can be attributed to the proximity effect at the Re₂O₇/graphene interface. In addition, states originating from O 2p can be observed in the valence band at energies around 5 eV and states (O-Re) which are a mixture of rhenium/oxygen states at energies around 8 eV below the Fermi level. Certainly, the observed work function for graphene on quartz modified with rhenium oxide confirms the possibility of using such a system as a transparent, conducting anode in OLEDs and photovoltaic cells. Analogous result of the increase in the graphene work function was obtained for Re₂O₇, which was deposited on bilayer graphene on SiC(0001) [5].

In the final step, a study of the Raman spectroscopy was carried out. This study was designed to evaluate the continuity of graphene layer on quartz and determine whether Re₂O₇ thermally applied to graphene surface causes defects in its structure. The Raman spectrometer (SOL Instruments) equipped with a 600 gr/mm diffraction grating and a 532 nm continuous-wave green laser (Coherent) at 5 mW with 50 times magnification objective (Zeiss) was used for the study. Figure 3 shows the Raman spectroscopy results of graphene on quartz after thermal deposition of Re₂O₇ with a thickness corresponding to a 50 nm layer. The spatial mapping mode with a size of 20 × 20 μm^2 was applied. The spectrum averaged from all 2500 spectra collected during the mapping is shown on the left. The following images show successively spatial maps of the intensity distribution for D-band (~1345 cm⁻¹), G-band (~1588 cm⁻¹), and 2D-band (~2685 cm⁻¹). The map for D-band shows the defect distribution of graphene after Re₂O₇ deposition. Raman spectroscopy studies clearly show (i) presence of only local graphene defects, (ii) thermal deposition of rhenium oxide does not defect graphene, and (iii) continuity of the layer is unaffected. Based on these observations, it is believed that such a layer is suitable for use as a transparent conducting electrode in optoelectronic devices.

3. Conclusions

In conclusion, the authors' study shows that the commercially available graphene transferred from copper foil to quartz, further modified with rhenium oxide meets the basic requirements for use as a conductive and transparent anode in optoelectronic devices. The results of AFM studies show that the thermal growth of rhenium oxide on graphene on quartz is cluster-like according to the

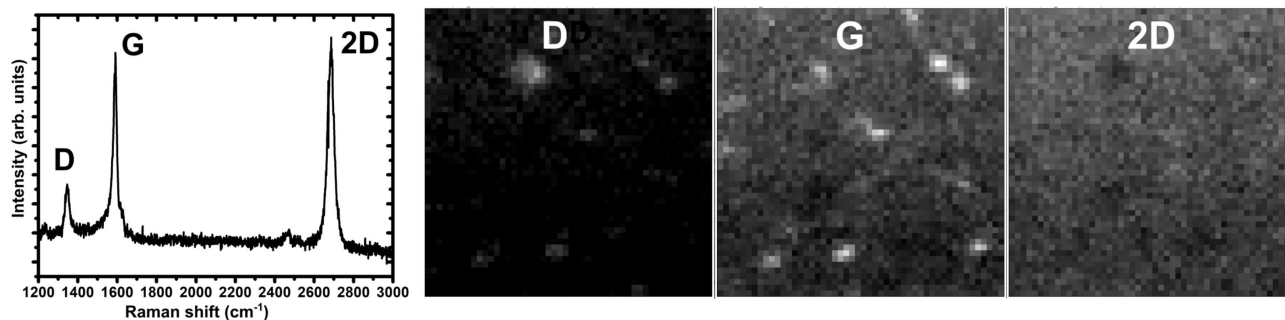


Fig. 3. Investigation of graphene on quartz after a thermal application of Re_2O_7 with a thickness corresponding to a 50-nm layer using Raman spectroscopy in a spatial surface mapping mode. A $20 \times 20 \mu\text{m}^2$ Raman map was collected with a resolution of 50×50 measurement points. On the left, the spectrum averaged from all 2500 spectra collected during the mapping is shown. Next, the spatial intensity distribution maps for the D, G, and 2D bands can be seen sequentially.

VW model. XPS studies have determined that the sample has a predominantly Re_2O_7 phase. UPS studies indicate that the work function of graphene can be easily modified by depositing Re_2O_7 . A very large increase in the work function for the modified graphene by as much as +1.3 eV to a level of 5.2 eV that is acceptable for use in real-world devices was observed. Raman spectroscopy studies indicate only local occurrence of defects after Re_2O_7 deposition. Intensive work is currently underway to use graphene deposited on quartz modified with Re_2O_7 as an anode in the OLED design.

Authors' statement

This article is a joint effort of a number of authors, in particular: research concept, design, AFM, XPS, UPS measurements, data analysis and writing the article, P.K.; Raman spectroscopy, Raman mapping, data analysis, M.P.; research concept and design, R.U., J.J., B.Ł., M.R., P.D.; design, J.C.; data analysis and interpretation, D.A.K., I.L., M.R., P.D., W.K., K.M., A.N., P.P., W.R., K.T., R.D., P.Kre., M.L.S., M.S.; critical revision of the article, B.Ł., J.U., P.J.K.; final approval of article, P.J.K.

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