Research Article

Layer-by-layer growth of molecular self-assembled monolayers /sputtered gold thin films/graphene oxide on glass substrate

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ARTICLE INFO

Article history:
Received 05 April 2020
Revised 27 April 2020
Accepted 10 May 2020

Keywords:
Graphene oxide
Heterostructure
Self-Assembly
Sputter deposition

ABSTRACT

In the present study, 1-dodecanethiol self-assembled monolayers (SAMs) on graphene oxide (GO) –Au (Gold) thin films as molecular templates for the selective deposition of multilayer films was performed. Thus, heterostructured GO/Au/DDT and DDT/Au/GO thin film are fabricated by sputtering Au target onto modified GO structure or self-assembled 1-dodecanethiol (DDT) arrays. It has been shown that a new device concept can be made by completing the glass substrate with the surface heterostructures; i.e. layer GO sheet or DTT with Au nanoparticles (Au NPs). In the light of the performed study, the layer-by-layer assembly of DDT on the GO sheet-Au thin films template has been proved for the distinct conjugation. Also, Optical and morphological characterizations are coherent with the instantaneous nucleation and growth model over the modified DDT-Au NPs-GO or GO-Au NPs-DDT thin films in the aspect of surface roughness, the phonon transport, and other multilayer films properties. As a consequence, the multilayer films of DDT-capped Au thin films and GO sheets have shown a better hybrid nanostructure with higher consistency, hierarchy and surface area. In addition, this work will present a new perspective for template preparation based on nanostructured thin films due to its unique properties resulting from nanoscale properties.

1. Introduction

In recent years, researchers have focused on layer improving on various surfaces to form a hybrid nanostructured continuous film. Hybrid nanostructures [1] have been paid attention due to their great potential applications in photocatalysis [2], biosensor production [3], magnetic materials [4-9] and super-hydrophobic materials [10]. These functional devices are continuously being developed by using advanced materials, they can be applied to high-tech applications [11]. With the use of SPM- based lithography [12-15] photolithographic techniques [16], molecular resist which is composed of a combination of sputter deposition and patterned monolayers has been used in a number of nanofabrication processes [17]. There are limited number of studies on the modification of graphene oxide (GO) compounds for pattern fabrication that use Au (Gold) thin films- self assembled monolayers (SAMs) as a resist. The patterned SAMs properties are used as a template for the sputter deposition of Au thin film layers or modification of GO. The inexpensive and simplicity of the present technique can allow to build a reachable implement of coordination of several multilayer films for electro-optical devices. The affecting of selective layer absorption using SAMs as a governing or directing surfaces introduces a new style of control in the formation of multilayers film systems [18]. GO is easily affected by reduction and doping. Thus, its application field has been continuously being developed [19] and it has been used for chemical and biomolecule sensor-based device production due to its p-type behavior in electron transition [20, 21]. In addition to this, Au nanoparticles (AuNPs) show great electrical conductivity, indicate controllability with their size,

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DOI: 10.35860/iarej.714811
shape, and surface-volume ratio and they can contain a great variety of ligands [22]. Thus, for decades, AuNPs have been employed for several high-tech applications involving sensors [23-25], optoelectronic devices [26] and drug delivery systems [27, 28].

In this study, self-assembly and sputtering process for layer-by-layer growth of GO, DDT, Au thin films were showed. In order to determine the composition, morphology and the structure, obtained films were examined by scanning electron microscopy (SEM), UV-vis spectroscopy, X-ray photoelectron spectroscopy (XPS) and Raman techniques.

Moreover, the information about nanostructured thin films which exhibits unique properties and could be used for applications in sensors was provided with this work.

2. Materials and Methods

2.1 Experimental

Argon were used as a sputtering gas while Au (99.99 %) was used as the target. The base pressure was < 3x 10^-4 Pa. In the process of deposition, with a sputtering power of 20 W, the substrate was kept at room temperature. After a deposition time between 25 sec-1000 sec, Au thin films with thickness that ranges from 80 to 200 nm were achieved. The experimental conditions were as follows: sputtering time 25 sec-1000 sec and applied voltage 20 W, respectively. GO (aqueous dispersion, 4 mg/mL) was purchased from Sigma Aldrich. 1-Dodecanethiol (DDT) SAMs were prepared by immersion of Au thin film-GO sheet in solutions containing 1 mM DDT (C_{12}H_{25}−S) (Fluka, purity ≥97%) for 24 h. Surface morphological studies of composites were examined and measured by scanning electron microscopy (SEM, Zeiss Sigma 300). WITech alpha 300R spectrometer was used to record Raman spectra of the composites over 4000~200 cm⁻¹. X-ray photoelectron spectroscopy (XPS) study was measured in a Specs-Flex XPS. Ultraviolet-visible (UV-Vis) spectroscopy measurements were obtained from a Shimadzu UV-3600 Plus spectrophotometer.

2.2 Results and Discussion

As can be seen in Figure 1, the general experimental strategy used in the present study included the synthesis of thin films that consist of GO sheets and the partial modification of DDT SAMs for producing etch centers with controlled sizes and implementation of sputter deposition of Au into those etch centers. With the sputter coater, the typical sputtering time was varied in the ranges of 25 sec-1000 sec. In all samples, the applied voltage was 20 W.

Figure 2a shows SEM micrographs of the Au films deposited on glass substrates as a function of sputtering time (20 W 100 sec sputter deposition). In these diagrams, the surface roughness and uniformly distributed Au grains were observed for the films.
The effect of sputter deposition time on the structure and the time of Au nanoparticle deposits are shown in Figure 3c without GO. In Figure 3d-e, SEM images are given as a function of different coating times of gold nanoparticles in GO-AuNP-DDT SAMs layers.

Figure 4 shows representative XPS high-resolution C1s and S2p core-level spectra in DDT SAMs-20 W 25 sec Au thin films and DDT SAMs-GO-Au NP. In especial, looking at the high-resolution XPS spectrum of S2p, it is possible to conclude that the functionalization occurred via S-Au chemical bond because of the presence of the components 157 eV. The 2p peaks were fit using doublet peaks with a 2p1/2/2p3/2 ratio of peaks 0.5 and separation of 1.3 eV as described previously. The first component, centered at about 157 eV, is assigned to the bound sulphur; the second one (at about 156 eV) is related to the presence of some unbound sulphur on the surface.

XPS had been applied to confirm the elemental composition and electronic states of DDT SAMs-20 W 25 sec Au thin films and DDT SAMs-GO-20 W 25 sec Au thin films in a wide scan. As displayed in Figure 4a, the DDT SAMs/Au nanostructures showed the elemental composition that appeared at approximately 283.3 eV at C-H, 283.8 eV at C-C and 284.5 eV at C-S which was attributed to the C1s core levels. Further investigations about the high-resolution XPS of the C1s showed three different components: C=C, C-H was at 283.7 eV, C=C, C-S at 284.5 eV, C-O appeared at 284.9 eV (Figure 4b), respectively.

Figure 5 shows the Raman spectra of DDT SAMs-20 W 25 sec Au NP, DDT SAMs-20 W 100 sec Au NP-GO, 20 W 1000 sec- DDT SAMs and GO-20 W 1000 sec-DDT SAMs.
Raman spectrum for the DDT SAMs-20 W 25 sec Au NP in Figure 5 shows weak G band at 1597 cm⁻¹ and a pronounced D band at 1382 cm⁻¹. The Raman spectra exhibit DDT SAMs-20 W 100 sec Au NP-GO at 1355 cm⁻¹ and 1602 cm⁻¹, respectively. In the peak S-band with shoulders at 1355 cm⁻¹ and 1602 cm⁻¹, corresponds to the G band of GO. There is no GO layer on the 20 W 1000 sec Au NP-DDT SAMs surface and therefore, the D and G belonging to the GO are not observed. G band intensity increased at 1605 cm⁻¹ due to the addition of GO when 20 W 1000 sec-DDT SAMs surfaces were modified to GO.

UV-visible absorption spectra of DDT SAMs-20 W 25 sec Au, DDT SAMs-GO-20 W 25 sec Au, 20 W 1000 sec Au—DDT SAMs and GO-20 W 1000 sec Au-DDT SAMs multilayer films on glass substrates are shown in Figure 6. An examination of the absorption spectrum at 300 nm spectral windows, which is quite similar to spectra reported for multilayer films. When GO is added to DDT SAMs-20 W 25 sec Au NP multilayer films, an increase in the absorption spectrum at 300 nm is observed. This is due to the increase in surface areas on the in DDT SAMs-GO-20 W 25 sec Au NP multilayer surface formed by the addition of GO. Furthermore, multilayer films produced by increasing Au NP deposition time cause an increase in the absorption spectrum of 300 nm when compared to other samples. When DDT SAMs-20 W 1000 sec Au NP multilayers films are modified on GO films, an increase in the absorption spectrum is observed. At a deposition time of 1000 sec, there was a 27 nm shift in its absorption edge as compared to the desorption time of 25 sec. It also caused differences in UV spectra in changing layers.

3. Conclusions

Finally, a new method has been figure out to fabricate the nanostructure array by combining the absorption layer of GO sheets and sputter deposition process using DDT SAMs as a resist. In the scope of the resist film, changing array of GO/Au thin film/DDT or DDT/Au thin film/GO, really important and promised nanostructure arrays with different morphological structures were achieved at the end of performed study. Also, the multilayer structures showed different extended morphology over a large surface area. The obtained results show that it is possible for us to propose that nanoporous templates have been used for the fabrication of nanostructured materials with potential applications for devices such as electronic, optical, magnetic and energy storage.

Declaration

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article. The author(s) also declared that this article is original, was prepared in accordance with international publication and research ethics, and ethical committee permission or any special permission is not required.

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