Journal of Colloid and Interface Science xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Self-assembly and nanosphere lithography for large-area plasmonic patterns on graphene

Valeria Lotito *, Tomaso Zambelli

Laboratory of Biosensors and Bioelectronics, Institute for Biomedical Engineering, ETH Zurich, Gloriastrasse 35, 8092 Zurich, Switzerland

ARTICLE INFO

Article history:
Received 25 September 2014
Accepted 4 November 2014
Available online xxxx

Keywords:
Self-assembly
Nanosphere lithography
Colloidal lithography
Plasmonic structures
Graphene

ABSTRACT

Plasmonic structures on graphene can tailor its optical properties, which is essential for sensing and optoelectronic applications, e.g. for the enhancement of photoresponsivity of graphene photodetectors. Control over their structural and, hence, spectral properties can be attained by using electron beam lithography, which is not a viable solution for the definition of patterns over large areas. For the fabrication of large-area plasmonic nanostructures, we propose to use self-assembled monolayers of nanospheres as a mask for metal evaporation and etching processes. An optimized approach based on self-assembly at air/water interface with a properly designed apparatus allows the attainment of monolayers of hexagonally closely packed patterns with high long-range order and large area coverage; special strategies are devised in order to protect graphene against damage resulting from surface treatment and further processing steps such as reactive ion etching, which could potentially impair graphene properties. Therefore we demonstrate that nanosphere lithography is a cost-effective solution to create plasmonic patterns on graphene.

© 2014 Elsevier Inc. All rights reserved.

1. Introduction

Graphene has emerged over the past years as a material with outstanding electrical, mechanical, thermal and optical properties that could potentially make it a suitable candidate to replace current technologies for a wide range of applications, going from electronics to optoelectronics and sensing [1–3].

From the preliminary studies of fundamental processes and pioneering device concepts, a real road map for possible functional device prototypes has been developed. Such headways have been fostered also by the progress of fabrication methods, such as chemical vapor deposition (CVD), which allow the availability of high quality large-area graphene for flexible electronics, large-area devices or complex device architectures and arrays, necessary, for example, for imaging devices requiring large arrays of photodetectors [3,4].

Despite the exceptional characteristics of graphene, there are still issues that need to be addressed to circumvent inherent limitations that could prevent its application to specific devices. An exemplary case is represented by graphene-based photodetectors. Such devices have been craving the attention of researchers over the past years because graphene offers large bandwidth and wide spectral range, differently from semiconductor photodetectors, which have a limited spectral width dependent on their bandgap. The wide spectral range is to be ascribed to the fact that the absorption spectrum of single layer graphene is almost wavelength-independent between 300 and 2500 nm [2]. However, the amount of absorbed incident radiation is approximately equal to $\pi\alpha \approx 2.3\%$ with α being the fine structure constant [1,2,5–7]: this value, even if impressive for an atomically thick layer, is still too low for a photodetector because it limits the photoresponsivity of the device to the order of fraction of mA/W [8–10]. With such a poor photoresponsivity, graphene-based photodetectors cannot be competitive with their semiconductor counterparts.

Plasmonic nanostructures on graphene have been demonstrated to increase the overall optical absorption of graphene, with a consequent enhancement of the photoresponsivity of graphene photodetectors by more than 20 times [9,11]. Basically two routes have been followed for the fabrication of plasmonic structures. The first approach is based on thermal annealing: more specifically, thermal annealing of a thin metal film sputtered on a Si/SiO_2 substrate results in the formation of a high density layer of plasmonic nanoparticles; afterward, polymethyl methacrylate (PMMA) is spin-coated onto the nanoparticles and a buffered oxide etching procedure is carried out to get a free-standing PMMA/nanoparticles film; after cleaning, the film is transferred on graphene and PMMA is dissolved to obtain plasmonic nanoparticles on graphene [9].

* Corresponding author.
E-mail address: lotito@biomed.ee.ethz.ch (V. Lotito).

http://dx.doi.org/10.1016/j.jcis.2014.11.007
0021-9797/© 2014 Elsevier Inc. All rights reserved.

Although a rough control over the size and density of the as-created plasmonic nanostructures can be achieved by varying some process parameters (such as the initial thickness of the metal film), a precise tuning of the characteristics of the final nanostructures is not feasible using this method, which means that the geometric and, hence, optical properties of these patterns cannot be accurately tailored. As an alternative, electron beam lithography (EBL) has been used to fabricate plasmonic structures with well-defined geometry [9,11]. Even if such a method offers better control over the shape and spectral properties of the final plasmonic patterns, it is intrinsically time-consuming and expensive and certainly not suitable for the creation of plasmonic structures over large areas.

The interest in creating plasmonic structures on graphene is not limited to photodetectors. Graphene has been suggested to be an excellent platform for plasmonic structures also for biosensors and chemical sensors as well as optical filters, reflectors, modulators, metasurfaces, surface enhanced Raman scattering, thanks also to the fact that the resulting plasmonic properties can be tailored by number of layers and tuned by electrostatic doping of graphene [12–18]. Moreover, it has also been suggested as an electrically tunable atomically flat dielectric spacer between plasmonic nanostructures and plasmonic substrate for high plasmonic field enhancement [12,19]. Also in these studies, plasmonic nanostructures were fabricated either by EBL [12,15], with the inherent drawbacks in terms of cost, time burden and area coverage, or by other methods (such as thermal annealing, seed-mediated growth, electrodeposition, self-assembly of nearly spherical gold nanoparticles followed by transfer on graphene [12,17–19]), resulting in random arrangements and limited control on shape and size of the final nanostructures.

Therefore the search for an approach that allows large-area fabrication of plasmonic patterns on graphene together with thorough control over the geometric and spectral characteristics of the plasmonic structures becomes essential. Here we propose the use of self-assembled hexagonal closely packed monolayers of polystyrene (PS) nanospheres as a template for the fabrication of plasmonic structures on graphene. These monolayers can be used as a mask for metal evaporation and etching processes in order to get regular patterns of diversely shaped plasmonic structures. An optimized apparatus has been designed to improve the quality of the self-assembled monolayers. In addition, controlled reactive ion etching (RIE) of the PS nanospheres can be used to further tune the characteristics of the final plasmonic patterns. Plasmonic arrays with long-range order and large area coverage are thus demonstrated on graphene.

2. Materials and methods

2.1. Materials

Nanosphere lithography was carried out on substrates consisting of monolayer graphene produced by CVD on copper catalyst and transferred to different substrates: 500 μm thick quartz and 525 ± 20 μm thick Si/SiO_2 substrate (with SiO_2 thickness of 300 nm). All the substrates were purchased from Graphenea. The size of the graphene substrates was $1 \times 1\ cm^2$ and graphene coverage was specified to be more than 95%. Aqueous suspensions at 10% solids by weight of PS nanospheres exhibiting high monodispersity (coefficient of variation less than 3%) were purchased from ThermoScientific (5000 Series polymer particle suspensions).

2.2. Nanosphere lithography on graphene

The traditional approach to nanosphere lithography consists in using a self-assembled monolayer of colloidal nanospheres (such as PS nanospheres) as a mask for deposition or etching [20,21].

Fig. 1 shows the two different processes. Typically, for a deposition process (Fig. 1(a)), the self-assembled monolayer of nanospheres is placed on the target substrate. The nanosphere diameter can be varied by RIE process. The desired material is then deposited, and, after nanosphere removal, the final structure consists of the deposited material exhibiting a regular pattern of nano-holes (if nanosphere diameter has not been reduced by RIE, the holes will be contiguous and the deposited material will take on the form of triangles created at the interstices between the nanospheres). In case of plasmonic structures, the deposited material can be a metal with plasmonic properties. For an etching process, the self-assembled monolayer is used as a mask to etch material not covered by the nanospheres. For example, the self-assembled monolayer is placed on the target substrate; nanosphere diameter can be varied by RIE; the material beneath the monolayer is etched away from the regions not covered by the nanospheres; finally, after nanosphere removal, nano-disks are obtained. If plasmonic nano-disks are desired, the self-assembled monolayer will be placed on a target substrate previously covered with a metal exhibiting plasmonic properties. Fig. 1(b) shows the process in case of a generic material previously deposited on the target substrate. The sketch of the nanostructures attainable with the described methods is shown in Fig. 1(c).

Although this approach has been successfully adopted for different material systems, it is not suitable for graphene. The reason for this is twofold. First, several self-assembly methods require the target substrate to be hydrophilic or to be made hydrophilic by specific surface treatments such as plasma cleaning; graphene wettability is still a controversial issue with some groups concluding that graphene is hydrophobic, even if this is sometimes attributed to airborne contaminations, others upholding the argument of complete or partial wetting transparency to some types of substrates, i.e. the dependence of the wetting properties on those of the substrate [22–25]. The second and most important reason is that some processes carried out to modify the colloidal mask are potentially harmful for graphene: for example, PS nanosphere etching is carried out by RIE in an oxygen based atmosphere, but this process would result also in graphene etching as it is usually done to shape graphene in different patterns [26,27]. Therefore the approach needs to be modified to be adopted for graphene.

We introduce a protective layer (indicated as material A) on graphene to prevent damage resulting from surface treatment and processing steps such as RIE. The outline of the process is shown in Fig. 2. In order to create nano-holes or nano-triangles, the self-assembled monolayer is placed on top of material A, previously deposited on the target substrate (in our case, graphene on Si/SiO_2 or quartz); if necessary, nanospheres undergo RIE and are then used as a mask for the evaporation of material B; finally, nanospheres and material A under the nanospheres are removed (left side of Fig. 2). For nano-disks, the self-assembled monolayer is put on the target substrate covered with material A and material B; nanospheres are used, after RIE, as a mask to etch material underneath (right side of Fig. 2). The approach is flexible and can be used for different material combinations (including also the same material as material A and material B), both dielectrics and metals (e.g. metals with plasmonic properties).

For the experiments reported in this article, deposition of materials on graphene was carried out using a Plassys II MEB550SL electron beam evaporator; RIE was performed with Plasmalab 80 (Oxford Instruments).

2.3. Self-assembly

Once the general outline for the process is defined, a proper strategy for the self-assembly of a hexagonal closely-packed monolayer of PS nanospheres needs to be devised. We carried out self-assembly

Please cite this article in press as: V. Lotito, T. Zambelli, J. Colloid Interface Sci. (2014), http://dx.doi.org/10.1016/j.jcis.2014.11.007

Download English Version:

https://daneshyari.com/en/article/606813

Download Persian Version:

https://daneshyari.com/article/606813

Daneshyari.com