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Characterization of graphene oxide nanofilms obtained by the SAW atomization

O V Balachova[1,4], S M Balashov[1], L T Kubota[2], R A Timm[2], P H Nascimento[1], A Pavani Filho[1] and S Moshkalev[3]

[1] Department of Microsystems, Center for Information Technology Renato Archer, Rod. D. Pedro I (SP-65), km 143.6, Amarais, Campinas-SP, 13069-901, Brazil
[2] Department of Analytical Chemistry, State University of Campinas, Campinas-SP, 13083-970, PO box 6154, Brazil
[3] Center for Semiconductor Components, State University of Campinas, r. João Pandia Calógeras, 90, Campinas-SP, 13083-870, PO box 6101, Brazil

E-mail: olga.balachova@cti.gov.br

Abstract. Due to its ability to absorb water molecules, graphene oxide (GO) is considered a promising material for sensitive coatings in fast surface acoustic wave (SAW) humidity sensors. In this work, we characterize GO films obtained by the SAW atomization technique. It is shown that the atomized submicroliter droplets of aqueous suspension of GO can be deposited onto the surface of Si, $LiNbO_3$ or quartz substrates forming discrete or continuous films of nanometer thickness. The deposited films were examined using AFM and electron microscopy. We discuss the dependence of thickness and structure of the obtained GO films on the parameters of deposition: the number of atomized droplets, a volume of the initial droplet, a distance between the atomizer and the sample, etc. To evaluate the adsorption characteristics of the obtained GO films, we used them as sensitive coatings of the SAW humidity sensors. We found that the adsorption characteristics of the GO films are determined by fast adsorption on the surface of GO sheets and slow adsorption, attributed to limited penetration of water molecules between the sheets, and depend on the number of deposited layers.

1. Introduction

Surface acoustic wave (SAW) sensors can be used for monitoring various chemical and physical parameters: strain, atmospheric pressure, humidity, biological matter, etc. [1-5]. The operating principle of these devices is based on a high sensitivity of the SAWs to the condition of the surface on which they propagate. For that reason some types of the SAW sensors–gas, biological, or humidity sensors–must have special coatings deposited onto the SAW propagation path between the interdigital transducers (IDTs) of the device. For example, thin films of polyvinyl alcohol (PVA) [2,3] and graphene oxide (GO) [4] find use as sensitive coatings for humidity sensors.

Thin GO films can be obtained from aqueous dispersions of GO with subsequent water evaporation by spin coating, spray coating or dip coating [6,7]. All these methods use large volumes of suspensions and have their limitations: spin coating, for example, cannot be applied for rectangular substrates, or very small substrates, or for the patterned film deposition. The drawback of dip coating

[4] To whom any correspondence should be addressed

and spray coating is that the obtained films are relatively thick. Also, evaporation of thick water layers can cause a significant non-uniformity of the final thickness of a film ("coffee-ring" effect).

To obtain thin GO films, we used the SAW atomization technique [4,8]. The idea of this method is to produce a very fine spray/aerosol from a single micro or submicroliter droplet of GO aqueous suspension and deposit it onto the surface of a substrate, where it will form a very thin wet layer. After evaporation of water, GO sheets will remain at the surface forming a very thin coating. The advantage of this method is that it allows controlling a volume of the atomized suspension and, therefore, a thickness of the deposited film. Another advantage is that it allows working with microvolumes of suspensions. Also, the SAW atomization can be applied for a patterned deposition of different films onto the surfaces of various shapes and dimensions.

In this work we study the dependence of thickness and structure of thin GO films on the parameters of the SAW atomization: the number of atomized droplets, a volume of the initial droplet, a distance between the atomizer and the sample, the applied RF power and sample surface preparation. Also, we evaluated the adsorption characteristics of the obtained GO films using them as humidity-sensitive coatings in the SAW sensors.

2. Experimental procedure

The graphene oxide films were deposited onto the surface of quartz, $LiNbO_3$ and Si substrates by atomization of 0.2 and 0.35-μl droplets of GO aqueous dispersions by the SAW atomization technique.

2.1. GO aqueous suspensions

First, graphite oxide was obtained from natural graphite by the modified Hummers' method. In our case, graphite (3.0 g) and $NaNO_3$ (1.5 g) were mixed with concentrated H_2SO_4 (69 ml) and cooled in an ice bath. A small amount of $KMnO_4$ was added to the obtained suspension. The suspension was heated for 30 min, cooled in an ice bath and diluted with DI water (138 ml, 18 MΩ·cm). Then, the suspension was left to react for 15 min at 98º C, cooled again and mixed with DI water (420 ml) and 30% H_2O_2 (3 ml). The final product was washed with H_2O, HCl and C_2H_5OH, then filtered and dried. The obtained material was dispersed in DI water (1 mg/ml) and exfoliated to GO in ultrasonic bath for 1 h. The obtained dispersion was diluted with DI water (1:1) and centrifuged at 1700 x g for 10 min. Immediately after centrifugation the supernatant was carefully removed with a pipette and transferred to a clean glass container. This procedure allows obtaining stable homogeneous GO dispersions that can be stored for few weeks without changing their properties.

2.2. SAW atomization

The SAW atomizing module is shown in the figure 1.

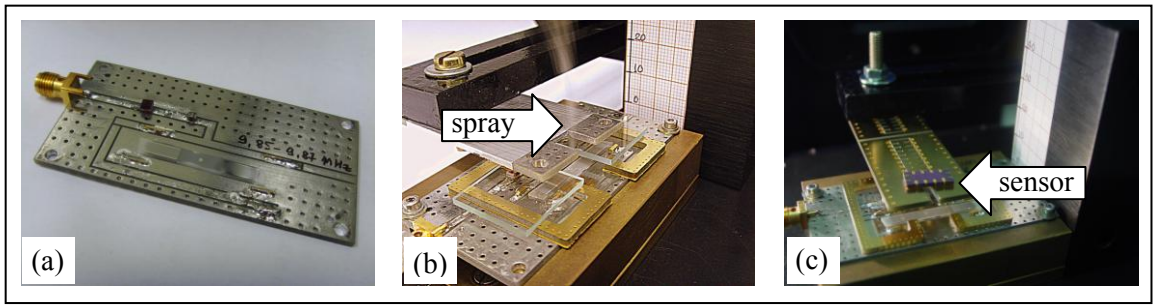

Figure 1. The atomizing module: SAW atomizer (a) in operation (b); the SAW humidity sensor (open active surface down) above the atomizer during atomization.

In this work we used the atomizers with symmetric IDTs fabricated on 128°-rotated Y-cut of $LiNbO_3$ by a conventional photolithography. Central frequency of the devices was 9.85 MHz. To atomize one droplet of GO suspension from the center of the atomizer, the RF signal was applied to the IDTs. The obtained aerosol was deposited onto the sample above the atomizer forming a thin coating. The atomization process took 1-2 s and water evaporation took about a minute. More detailed description of the SAW atomization technique can be found elsewhere [4,7].

3. Results and discussion

Although the GO aerosol obtained by the SAW atomization of submicroliter droplet can spread on large areas (up to 15 cm^2), the resulting film is not uniform (figure 2a): its thickness decreases noticeably from the center to borders (figures 2b and 2c). Only a central part of the film (in our case, it is a circle of 2.5 mm in diameter, approximately) can be considered uniform. This region is situated directly above the center of the atomizer during deposition and obtains a maximum amount of graphene oxide with aerosol.

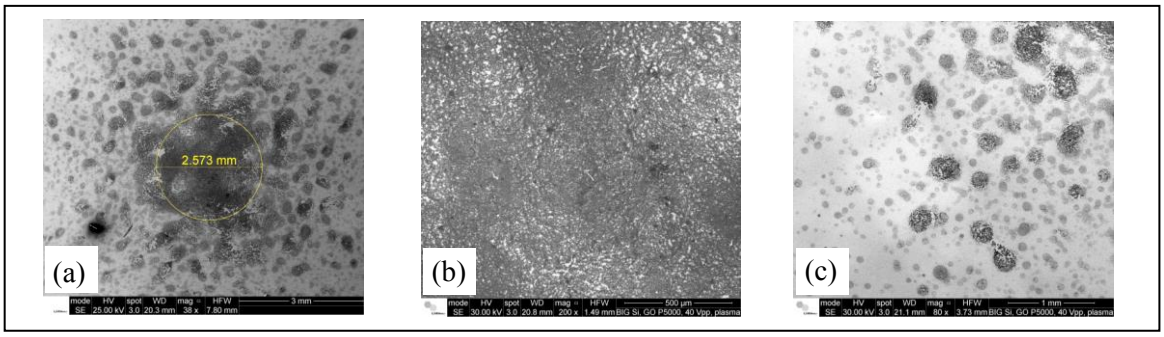

Figure 2. GO film on the Si surface: general view (a), the central spot (b) and the border (c).

The dependence of the thickness of GO films on the number and volume of atomized droplets is shown in the figure 3 and figure 4. It can be seen that thicker films are obtained by increasing the number of atomizations and/or by atomizing larger droplets, keeping constant the other parameters of the process. Adjusting the parameters of the process, it is possible to obtain continuous uniform coatings.

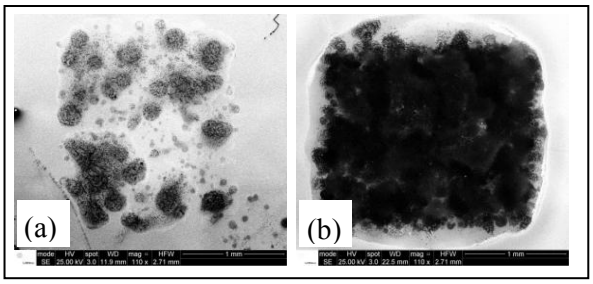

Figure 3. GO films at the silicon: one (a) and ten (b) depositions of 0.2-µl droplets.

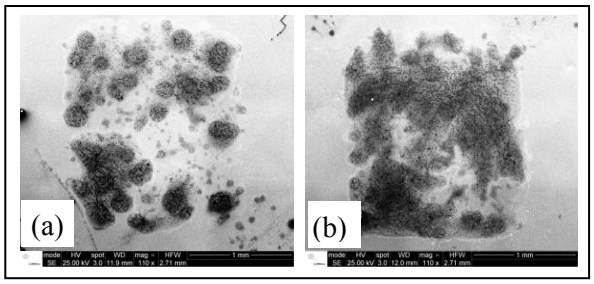

Figure 4. GO films at the Si: one deposition of 0.2-µl (a) and 0.35-µl (b) droplets.

Another parameter that influences the quality of the film is the distance between the atomizer and a sample: more uniform films were obtained at 6-9 mm from the atomizer surface. Also, thicker GO films with higher degree of surface coverage were obtained at higher RF power for the same parameters of the process (figure 5).

We observed more uniform coatings and higher degree of coverage at the surfaces activated in oxygen plasma before the film deposition (15 min at 100 W and 200 mTorr) for all substrates (figure 6). SEM images demonstrated that after one or two depositions a substantial area of the coatings is formed by single or double GO sheets (figure 7). AFM measurements showed that the thickness of the

films in this case is about 2.5-3 nm. The films deposited onto the non-activated by plasma samples (figure 6a) are much thicker: 40-100 nm after one deposition. It results from the fact that activated surfaces ensure better spreading of the deposited spray droplets before drying.

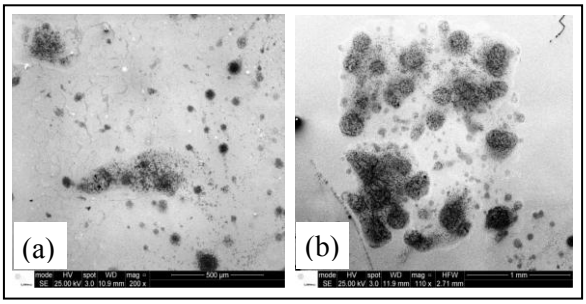

Figure 5. GO films on the Si surface: 1 W (a) and 4 W (b) of the applied power.

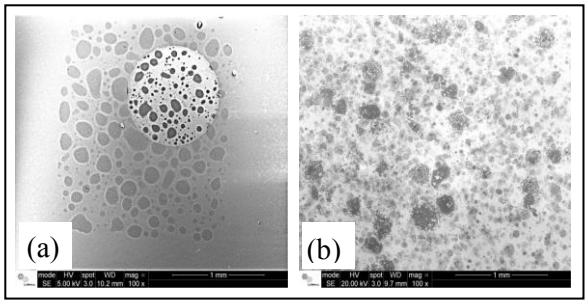

Figure 6. GO films on $LiNbO_3$: no surface activation (a) and after surface activation (b).

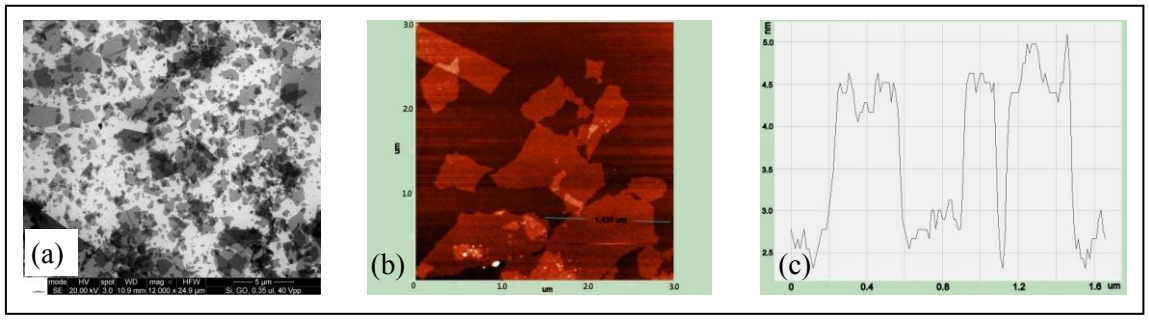

Figure 7. GO film: SEM image (a), AFM image (b) and thickness measurements (c).

4. Adsorption characteristics of GO films

To evaluate the adsorption characteristics of the obtained GO films, we used them as sensitive coatings of the SAW humidity sensors. We monitored the kinetics of evaporation of water molecules from the surface of the liquid sample of saturated salt into the enclosed chamber with initially zero relative humidity. The details of these experiments can be found elsewhere [4,9]. Typical experimental differential frequency response of the sensor $f(t)$, shown in the figure 8, was approximated by the multi-exponent equation, which corresponds to N adsorption processes

$$f(t) = F_0 + \sum_{i=1}^{N} A_i(1 - \exp(-\alpha_i t)) \quad (1)$$

where F_0 is a baseline differential frequency, which corresponds to the response of the sensor at the initial moment, when relative humidity is equal to zero; A_i and α_i are the correspondent saturation amplitude and rate coefficient [10,11]. The results of LSQ-fitting of typical experimental data with (1) for N=1 and N=2 (figure 8) demonstrate that the approximation with N=2 is more appropriate. The values of A_i and α_i (i=1,2) for a wide range of humidity are presented elsewhere [4]. The analysis of these data shows that the saturation time (rate coefficient) of the first process is approximately ten times smaller (bigger) then of the second one. The first process (i=1) can be attributed to the process of evaporation of water molecules from the surface of the liquid sample and their adsorption by the sites on the surface of the GO sheets. These sites have the lowest adsorption energy and, hence, the smallest adsorption time. The second process (i=2) can be attributed to the adsorption on the border of GO sheets or between them. The response time of the sensor grows with the number of deposited films due to a higher degree of surface coverage by GO and a larger number of adsorption sites.

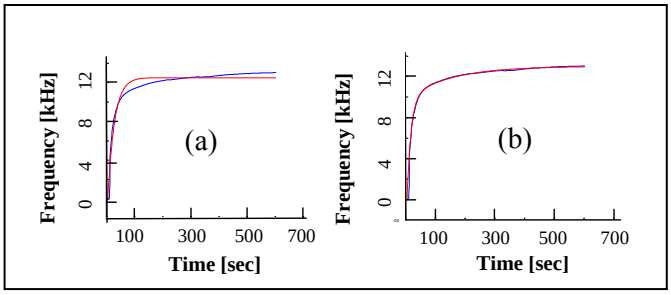

Figure 8. Typical experimental kinetic adsorption curve (blue) of the GO SAW humidity sensor. Red curves represent its LSQ-fitting results with (1) for N=1 (figure 8a) and N=2 (figure 8b).

5. Conclusions

The SAW atomization technique can be used for patterned deposition of GO films from aqueous GO suspensions onto the surface of different substrates including quartz used in the SAW humidity sensors. The films form discrete or continuous coatings at the surface of the substrates/sensors with the minimum thickness of 2.5-3 nm which corresponds to a GO monolayer. The thickness of the deposited films strongly depends on the number of atomized droplets, a volume of the initial droplet, a distance between the atomizer and the sample, the applied RF power and sample surface preparation and can be controlled. Discrete coatings can be obtained by a small number of the atomized droplets, but to obtain the continuous coatings, it is necessary to make at least 10 depositions. The thickness of the films remains constant in its central area of 2.5 mm in diameter approximately. Water adsorption is determined by the fast process on the surface of GO sheets and the slow process attributed to the limited adsorption between GO flakes and grows with the number of deposited layers.

Acknowledgements

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