Contribution (Oral/Poster/Keynote)

Oxygen and deuterium incorporation in graphene on SiO_2/Si substrates

N. M. Bom[1,2], G. V. Soares[3,4], M. H. Oliveira Jr.[1], J. M. J. Lopes[1], H. Riechert[1], C. Radtke[4]

[1]Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5-7, 10117 Berlin, Germany; [2]PGMICRO, UFRGS, 91509-900 Porto Alegre, Brazil; [3]Instituto de Física, UFRGS, 91509-900 Porto Alegre, Brazil; [4]Instituto de Química, UFRGS, 91509-900 Porto Alegre, Brazil

bom@pdi-berlin.de

Owing to its unique properties with respect to charge transport, graphene is one of the most promising contenders for future nanoelectronic devices. However, the processing and modification of graphene properties for technological purposes is still a challenge. In this context, adsorption in graphene is of central importance. It has been already reported that oxygen (O) and hydrogen (H) incorporation in graphene layers have a strong influence in their transport and structural characteristics [1,2]. Therefore, understanding the interaction of H and O species with these structures and related chemical modifications are fundamental issues. In the present work, we investigate the incorporation of H and O in graphene layers upon water vapor (H_2O) annealings.

Starting samples consisted of monolayer graphene grown by chemical vapor deposition (CVD) on copper and then transferred to SiO_2 films (285 nm thick) on Si. Bare SiO_2 films of the same thickness on Si were also submitted to the same experiments for the sake of comparison. Samples were loaded in a static pressure and resistively heated quartz tube furnace, which was initially pumped down to 2 x 10^{-7} mbar. Hereafter, they were annealed at temperatures ranging from 100 up to 1000 ºC, for 1 h, in a 10 mbar H_2O atmosphere enriched in the ^{18}O and ^{2}H (D) rare isotopes. These isotopes were chosen in order to distinguish O and H incorporated during experiment from those incorporated due to air exposure and/or from the SiO_2 film. As references, samples annealed at the same temperatures but in UHV were also investigated. ^{18}O and D quantification were accomplished by nuclear reaction analyses (NRA), using the $^{18}O(p,\alpha)^{15}N$ nuclear reaction [3] at 730 keV (10^{13} $^{18}O/cm^2$ sensitivity and 5 % accuracy) and the $D(^3He,p)^4He$ nuclear reaction [4] at 700 keV (10^{12} D/cm^2 sensitivity and 5% accuracy), respectively. In addition, Raman scattering and X-ray photoelectron spectroscopy (XPS) were employed for the characterization of the graphene.

Figure 1(a) shows the D areal density as a function of $D_2{}^{18}O$ annealing temperature for graphene/SiO_2/Si and for SiO_2/Si. At 100 ºC D incorporation is observed, which is similar for both samples. In the 200 - 400 ºC temperature range, a higher incorporation in the graphene coated sample is observed in comparison to the bare SiO_2. The D amount difference between these samples is shown in the inset (blue triangles). In this range of temperature we observe 1 x 10^{15} D/cm^2 in graphene, which is independent of the temperature and corresponds to about a monolayer of D. Since graphene films are polycrystalline, D may be incorporated at the graphene grain boundaries which can be sites for hydrogen incorporation. For 600 ºC annealed samples, we start to observe a decrease in the D incorporation while the opposite is observed for the bare SiO_2. This result suggests that D bonded to graphene is not stable above 400 ºC, similarly to D bonded to Si dangling bonds at the SiO_2/Si interface.

^{18}O areal density as a function of $D_2{}^{18}O$ annealing temperature for graphene/SiO_2/Si and SiO_2/Si are shown in Fig. 1(b). Since both samples offer a 285 nm thick SiO_2 film, one can use the relation 1 x 10^{15} O/cm^2 ⇒

0.226 nm to determine the corresponding amount of oxygen in the SiO_2 film. Considering the natural abundance of ^{18}O (0.2 %), this amount is about 2.5 x 10^{16} $^{18}O/cm^2$. Similarly to D, in the 200 – 400 ºC range, a higher incorporation of ^{18}O is observed for the graphene-covered samples. However, by further increasing the annealing temperature (600-1000 ºC), the ^{18}O incorporation rate in bare SiO_2 becomes larger than the one measured for samples covered by a monolayer graphene. The reason for this is twofold: first, at 600 ºC we start to observe the oxidation of the Si substrate and formation of additional SiO_2; second, exchange between ^{16}O from the SiO_2 and ^{18}O from the gas phase may also occur. However, the incorporation is less pronounced in graphene as it may act as a diffusion barrier [5] for oxygen, reducing the incorporation/oxidation of the Si substrate and the isotopic exchange.

Corroborating these results, XPS measurements (not shown) identify the formation of C-O and C=O bonds. In the 200-400 ºC range, the C1s components can be associated to oxygen incorporation, indicating that water may react with graphene forming oxygen-carbon bonds, and that it can also be incorporated as OH groups. On the other hand, between 600-1000 ºC one can observe components in a new bonding configuration, which may occur due the partial removal of the graphene layer and the formation of defects. Finally, Raman scattering spectroscopy and magneto transport measurements (van der Pauw geometry), which were employed in order to investigate the structural and electrical properties associated to the observed physico-chemical modifications, will be presented.

References

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Figure

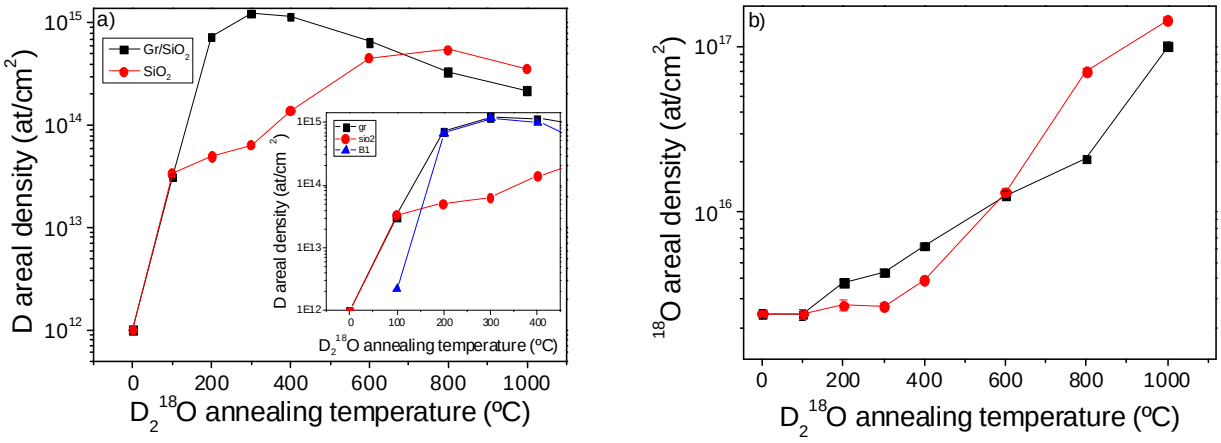

Figure 1 - Areal densities of D (a) and ^{18}O (b) as a function of $D_2{}^{18}O$ annealing temperature for graphene/SiO_2/Si (black squares) and SiO_2/Si (red circles). Inset: Areal densities in the 0-400ºC temperature range. Blue triangles stand for the difference between D or ^{18}O incorporated in graphene and SiO_2. Lines are only to guide the eyes.