Monolayer Graphene, a perfect hub for the study of out-of-equilibrium phenomena in plasma-surface interactions

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Abstract: Plasma-surface interactions understanding is crucial for various applications but still lacking clarity in several aspects. The influence of hyperthermal ions generated by low-pressure plasma on defect generation at materials' surfaces is not clearly understood. In this context, monolayer graphene is an ideal material to explore such phenomenon occurring at the extreme surface. A combination of experiments and simulations shows how ion neutralization transfers a non-negligible amount of energy enabling defect generation.

Keywords: plasma-surface interactions, monolayer graphene, defects, argon plasma, hyperthermal ions

1. Introduction

With the ever-decreasing dimensions of semiconductor devices, the precise understanding of plasma-surface interactions becomes crucial. It is especially necessary to study how low-pressure plasma can generate defects despite the low-energy ions, which can be used in certain processes [1]. Upon contact with the sample, plasma excited species generate out-of-equilibrium phenomena on surfaces, of which influences are difficult to quantify. Furthermore, synergistic phenomena can arise with the simultaneous irradiation of the sample by other plasma-excited species such as metastables and V-UV photons[2]. These effects are often invoked but hardly understood. As a result, a mechanistic understanding of plasma-surface interactions involving all excited species remains a challenge.

Since its experimental discovery in 2004 [3], tremendous research effort worldwide has been focused on monolayer graphene to harness its remarkable properties. There are now numerous characterization methods that enable a precise understanding of its structure. Among them, Raman spectroscopy is particularly successful in providing a clear view of the concentration and nature of defects without altering the graphene state [4]. Graphene is particularly affected by any surface treatment, making it ideal for the observation of phenomena affecting the top surfaces of materials in general.

It has been shown that low-pressure argon (Ar) plasma irradiation of graphene induces a significant number of defects despite the ultralow energy (hyperthermal) ions (~10-13 eV) [5]. This is even more remarkable, considering that the threshold energy to generate defects in graphene is well established as 18-20 eV [6]. This research aims to explain how the neutralization of hyperthermal ions at surfaces may contribute to defect generation by introducing supplementary energy input.

2. Defect density determination

Raman spectroscopy revealed itself to be a non-invasive tool to probe graphene states and determine the defect density as well as doping and strain levels[4]. Figure 1 shows typical Raman spectra of untreated and Ar plasma-treated monolayer graphene samples.

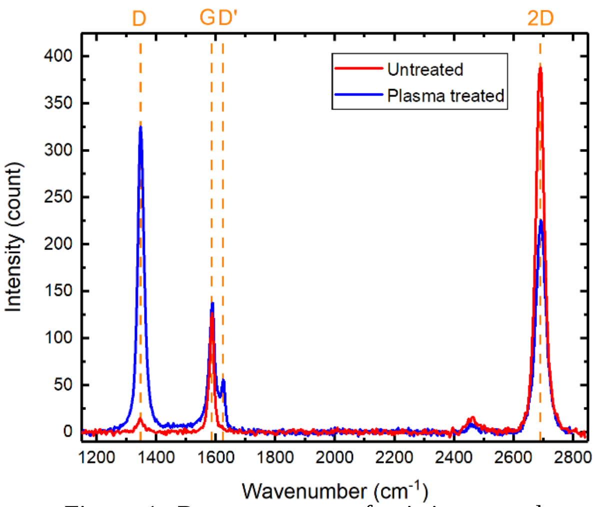

Figure 1: Raman spectra of pristine monolayer graphene (red) and plasma-treated graphene (blue).

The red curve presents two main peaks, the 2D peak at 2700 cm^{-1} and the G peak at 1580 cm^{-1}. The former is typically very intense for high-quality monolayer graphene while the last is present for all carbon (C) materials. The blue curve shows two supplementary peaks, namely the D peak at 1350 cm^{-1} and the D' peak at 1610 cm^{-1}. Both are defects activated and are observed when defects such as vacancies are present in the graphene lattice. In this case, monolayer graphene on SiO_2 has been exposed to a low-pressure Ar inductively coupled plasma (ICP), which induced a significant rise in defect density despite the very short treatment time (21s) [5].

A typical approach to assessing the defect density from Raman spectra relies on the intensity ratio of the D peak over G (I_D/I_G). Ferriera *et al.* [7], [8] demonstrated that

I_D/I_G increases linearly with the defect density in the low-defect density regime.However, this ratio is influenced by other factors such as the doping or strain level of graphene, hindering proper extraction of defect density values. To circumvent this issue, another intensity ratio can be used such as I_D/I_{2D} as it is much less affected by doping or strain. Figure 2 presents the evolution of both I_D/I_G and I_D/I_{2D} as functions of the defect density extracted from the initial report of Ferriera *et al* [7].

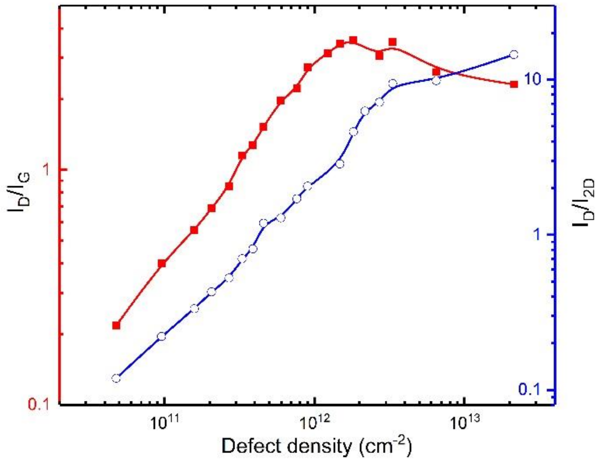

Figure 2: Evolution of I_D/I_G (red full square, left axis) and I_D/I_{2D} (blue empty circle, right axis) as a function of defect density obtained with the data from [7].

The I_D/I_G ratio shows a linear increase with the rising defect density up to ~ 10^{12} cm^{-2}, which can be considered as the limit before amorphization. Further defect generation will provoke a decrease in this ratio. The I_D/I_{2D} ratio also shows a monotonic rise, which continues up to a higher defect density than I_D/I_G (~2×10^{12} cm^{-2}). Therefore, as shown in Fig. 2, I_D/I_{2D} varies linearly with the defect density and would be better suited to estimate the defect density in monolayer graphene to avoid interdependencies with graphene's doping or strain level.

3. Ion Energy fluence influence

To better understand plasma-surface interactions, it is necessary to determine first the influence of each energetic species. In doing so, ion bombardment studies are pertinent, which can be compared with plasma experiments. However, it is technically challenging to produce hyperthermal ions with kinetic energy below 15 eV. Nevertheless, one study reported defect generation in monolayer graphene by Ar ions with energy as low as 10 eV [9]. It is then of interest to compare the amount of defect generated by plasma with that by 10 eV, and 90 eV ion irradiations [7], [10]. Figure 3 presents the evolution of I_D/I_{2D} as functions of energy fluence during Ar ion bombardment at 10eV, 90eV, and an Ar plasma treatment generating 10-13 eV ions.

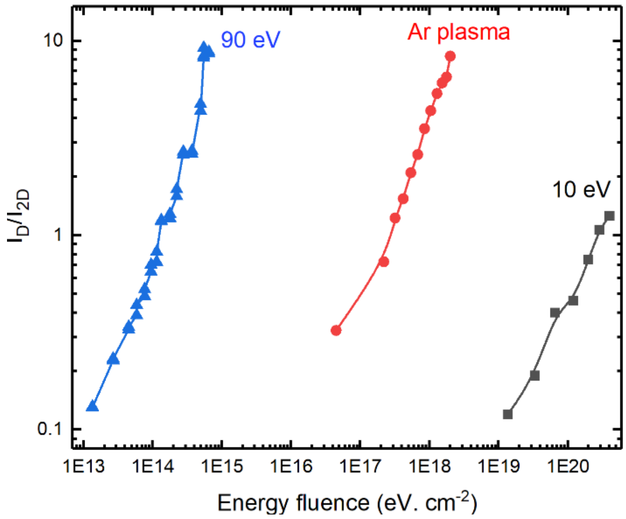

Figure 3: Evolution of I_D/I_{2D} as functions of energy fluence resulting from the irradiation of 90 eV ions (blue triangle), a plasma containing 10-13 eV ions (red circle) and 10 eV ions (black square) on monolayer graphene.

In all three cases, a similar monotone increase is observed with the energy fluence. While I_D/I_{2D} values are close, large discrepancies are visible in energy fluence absolute values. In the case of 90 eV ions, energy fluence varies from 10^{13} up to 7×10^{14} eV.cm^{-2} while it varies between 10^{19} and $4\text{x}10^{20}$ eV.cm^{-2} in the 10eV case. Meanwhile, energy fluence varies from $2\text{x}10^{16}$ eV.cm^{-2} up to 10^{18} eV.cm^{-2} for the plasma treatment. Such drastic differences among different experimental conditions can be linked to a probability of defect generation that depends on the ion energy. Indeed, based on the threshold energy reported in the literature, Ar ions should not generate defects below a kinetic energy of 30 eV. Nevertheless, defects can indeed be generated with 10 eV ions. Considering how slopes are similar in all cases, similar defects are suggested to be generated with a much lower probability compared to 90 eV ions. Since the ions' kinetic energy is not sufficient by itself to generate vacancy, a supplementary energy input must be provided. Hyperthermal ions are expected to transfer part of their potential energy as they neutralize on the surfaces (up to 15.8 eV). Furthermore, this energy would be provided close to the point of impact shortly before the actual collision. Consequently, the ion neutralization could effectively decrease the threshold energy for defect generation. To better understand the influence of such energy input, molecular dynamics (MD) simulations are pertinent as they are often used to study defect generation dynamics [11].

4. MD simulations

Classical MD simulations were carried out with the open-source code LAMMPS. In the simulations, suspended graphene was exposed to ions at different energy from 10 eV to 90 eV. To emulate the energy input from ion neutralization, we heated graphene at 3000K. It should be noted that this is a crude approximation of the transitionary state of graphene resulting from ion neutralization and does not reflect the actual temperature of graphene in experiments. A three-body ZBL/Tersoff potential function was used to model graphene while a Lenard-Jones potential was used to estimate Ar-C interactions in a similar manner as Bellido *et al* [11]. 50ps-long simulations were carried out 500 times to obtain sufficient statistics. Figure 4 presents the defect formation probability as functions of the incident energy of Ar ions on graphene at room temperature and 3000K. Adatom generation (when an atom removed from the lattice stays on the graphene surface) is distinguished from sputtering.

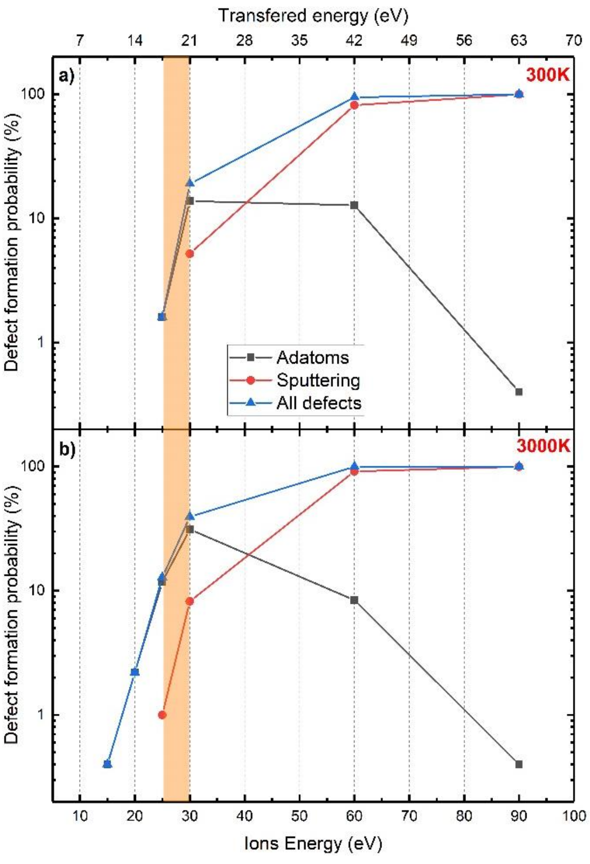

Figure 2: Evolution of the defect formation probability of adatoms (black square), sputtering (red circle), and the sum of both (blue triangle) as a function of ions initial kinetic energy in the case of a) graphe ne at room temperature and b) graphene heated at 3000K

At 300K, the adatoms defect probability is nonzero above around 18-20 eV, which is the threshold energy for defect generation reported in the literature. Sputtering takes place above around 30 eV and its probability increases with ions energy while the adatoms probability sharply decreases. Ions at 90 eV mainly produce sputtering, as observed by Ferreira et al [6]. In the 3000K case, adatoms can be generated above around 15 eV, instead of the 25 eV threshold energy obtained at 300K. Similar behavior can be observed for sputtering, appearing at 18eV instead of 20eV, but becoming even more dominant at higher energy. Therefore, a supplementary energy input in the form of thermal energy decreases the threshold energy for defect formation. This is consistent with density functional tight-binding simulations which showed a “broadening” of the displacement threshold energy with temperature [12]. Experimentally, this would translate into a decrease in the threshold energy as well. However, the probability is low and such phenomena require higher energy fluence to be observed in experiments. This agrees with the previous analysis comparing the energy fluence in different conditions. Furthermore, graphene has been reported to self-heal by C adatoms. This could reduce significantly the defects density determined experimentally in the case of hyperthermal ion irradiations producing mainly adatoms.

5. Conclusions

The potential of graphene to provide a deeper understanding of plasma-surface interactions has been discussed. Comparison of the defect generation by ion irradiation at different ion energies with that by plasma irradiation enables us to obtain an insight into the influence of hyperthermal ions on defect generation. Even though with a low probability, defect generation by such ions is possible because they have a high probability of neutralizing themselves when in contact with surfaces. This is confirmed by classical MD simulations of graphene heated at a higher temperature, representing the local energy input before the actual collision. On the other hand, hyperthermal ions are more likely to generate adatoms that can diffuse and potentially heal vacancies afterward, reducing the defect density estimated experimentally.

These results call for further studies to clearly understand how an incident ion’s potential energy is transferred to graphene before impinging on the surface. It would be also of great interest to better understand the influence of Ar metastable and VUV photons on surfaces, which have been reported to have a non-negligible impact on the defect-generation kinetics of graphene [2].

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