Comment on "Interfacial Carbon Nanoplatelet Formation by Ion Irradiation of Graphene on Iridium(111)"

■ In a recent article by Herbig *et al.*,[1] some of us reported the formation of bulges in a graphene (Gr) sheet on Ir(111) after conducting Xe^+ irradiation (energy range of 0.1−5 keV) at 300 K and subsequent annealing to 1000 K. Additional X-ray photoelectron experiments after irradiation and annealing now invalidate the following assessment in the article: "We also rule out that the bulges are agglomerations of implanted noble gas atoms. Although noble gas is certainly implanted into the Ir crystal, trapped in bulk vacancies as well as bulk vacancy clusters, and partially released during annealing to 1000 K, the Gr cover will not protect it from desorption." Our additional experiments show that indeed the Gr cover protects Xe efficiently from desorption.

In a first experiment, we exposed the bare Ir(111) sample to 3 keV Xe^+ at 300 K and conducted successive annealing to 1000 and 1300 K. The ion fluence selected was 0.1 MLE, where 1 MLE is 1.57×10^{19} ions/m^2, that is, numerically identical to the surface atomic density of Ir(111). After irradiation at 300 K, the bottom spectrum in Figure 1a displays an Ir 4s core level peak together with the Xe $3d_{3/2}$/Xe $3d_{5/2}$ core level doublet. Since Xe only physisorbs on Ir(111), consistent with desorption around 100 K and a binding energy of 0.21 eV as obtained by our density function theory (DFT) calculations, the Xe 3d signal after irradiation must be attributed to Xe implanted into the Ir sample. Upon annealing to 1000 K and subsequently to 1300 K, the Xe signal diminishes (compare middle and top spectra in Figure 1a, as well as solid squares in the inset). We explain these changes as follows: due to thermal excitation, Xe is partially released from its trapping sites inside the crystal, diffuses to the surface, and desorbs to the vacuum, consistent with our statement in ref 1. The residual Xe signal after annealing to 1300 K is due to Xe aggregates trapped in bulk vacancy clusters, as found also in previous studies for similar systems.[2,3]

Conducting precisely the same irradiation experiment, but for Ir(111) covered by a complete monolayer of Gr, yields very different photoelectron spectra, as shown in Figure 1b. Already after ion exposure at 300 K (bottom spectrum of Figure 1b), the integrated Xe 3d intensity is higher by a factor of 2 compared to irradiation of bare Ir(111) (see also inset of Figure 1a). All of the additional intensity must be due to Xe trapped between the Gr cover and the Ir substrate. Annealing to 1000 and 1300 K leads to a slight increase and a substantial increase, respectively, of the integrated Xe 3d peak intensity. The interpretation is straightforward: Instead of being released to the vacuum, the Xe diffusing out from the Ir bulk becomes trapped under the Gr cover and thereby enhances the Xe 3d intensity (smaller photoelectron attenuation due to smaller depth). By comparison with the Xe 3d signal of a saturated Xe 3d monolayer adsorbed to Ir(111), it is found that

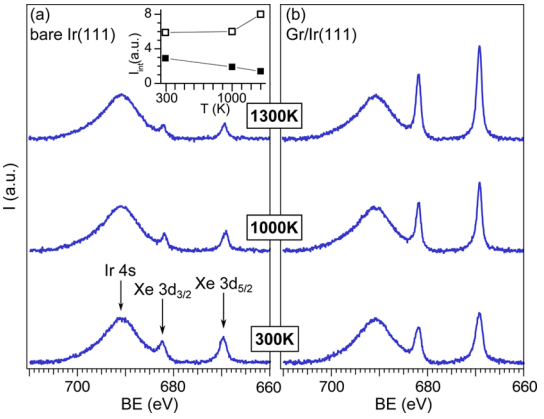

Figure 1. X-ray photoelectron spectra of the Ir 4s, Xe $3d_{3/2}$, and Xe $3d_{5/2}$ core levels for (a) bare Ir(111) and (b) Gr-covered Ir(111) after normal incidence exposure to 0.1 MLE of 3.0 keV Xe^+ at 300 K and annealed to stepwise increasing temperatures, as indicated. The intensity, *I*, is plotted as a function of core level binding energy (BE). Spectra are collected in normal emission with a photon energy of 1000 eV and a total energy resolution better than 400 meV, background subtracted, and normalized to the Ir 4s peak height. Inset: Integrated Xe $3d_{5/2}$ intensity, I_{int}, as a function of temperature for exposure of bare Ir (solid squares) and Gr/Ir(111) (open squares).

the amount of trapped Xe is on the order of 10% of a saturated Xe layer. The efficient trapping of Xe during room temperature irradiation and subsequent annealing is remarkable since (i) a Xe atom does not bind chemically to Ir(111) or to Gr/Ir(111) (DFT binding energy 0.17 eV) but instead causes a DFT-calculated energy penalty of 2.9 eV in the trapped state due to elastic deformation of the Gr on Ir(111); (ii) the Gr cover was heavily damaged and partially sputtered (about 15% of the Gr area is removed according to the sputtering yield obtained from our molecular dynamics simulation); and (iii) the perfect Gr layer adheres only weakly to the substrate with an average height of 3.4 Å.[4] The latter two factors make the situation different from two previously reported cases,[5,6] where trapping was observed in the limits of very small fluence and very low energy (marginal damage and sputtering) and for strong adhesion of the 2D material to the substrate [a monolayer of hexagonal boron nitride on Rh(111) and Gr on Ru(0001)].

Given the large amount of Xe trapped under Gr, it appears that the bulges observed in ref 1 are formed predominantly due to Xe aggregates rather than interfacial Gr nanoplatelets as was proposed by Herbig *et al.* In light of the experiments reported here, bulges observed by Herbig *et al.* after 0.3 keV Ne^+ or Ar^+ room temperature irradiation and 1000 K annealing are most likely due to trapped Ne or Ar.

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