Structure and dynamics investigations of a partially hydrogenated graphene/Ni(111) surface

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ABSTRACT

Using helium-3 atom scattering, we have studied the adsorption kinetics, the structure and the diffusional dynamics of atomic hydrogen on the surface of a graphene monolayer on Ni(111). Diffraction measurements reveal a 4° rotated rectangular hydrogen overstructure. Hydrogen adsorption and desorption exhibit activation barriers of $E_a = (89\pm7)$ meV and $E_d = (1.8\pm0.2)$ eV, respectively. Helium-3 spin-echo measurements showed no decay of the spatial correlation function (or intermediate scattering function) within the time range of the spectrometer. Hence, we are able to set lower limits for a possible hydrogen surface diffusion rate.

1. Introduction

The existence of an ordered hydrogenation of graphene remains an open question to date although it is of fundamental interest for the tuning of graphene properties [1]. The existence of a stable fully hydrogenated graphene [2,3] layer (graphane) was theoretically predicted almost a decade ago [4], but the synthesis of an almost perfect graphane layer has only recently been reported [5]. A review on graphane and hydrogenated graphene has been published by Pumera et al. [6]. In perfect graphane, one hydrogen atom binds to each carbon atom in an sp^3 hybridised state in an alternating manner, with the hydrogen atom being located either above or below the 2D plane. This leads to four different possible conformations: the chair, boat, twisted-chair, and twisted-boat conformations [6].

The first successful hydrogenation of graphene was reported by Elias et al. [7], where free-standing graphene and graphene on a SiO$_2$ substrate were used. On top of a substrate, only single-sided hydrogenation of graphene is possible, which has been predicted to create a disordered material [7]. A graphene layer that is fully hydrogenated on one side is being referred to as graphone. Graphone has recently been successfully synthesised from graphene/Ni(111) in a reversible manner [8]. The partial one-sided hydrogenation of a graphene sheet has also recently been achieved by splitting of intercalated water in the graphene/Ni(111) system at room temperature [9].

Before the theoretical discovery of graphane and graphone, the hydrogenation of the graphite(0001) surface had been studied intensely for various interests, such as the mechanism of H$_2$ formation in the interstellar medium. A disordered formation of hydrogen dimers on graphite was observed at low hydrogen coverage [10,11], while at high coverage the appearance of a triangular structure was observed that occupies only one of the two trigonal sublattices, into which the (0001) surface can be separated [12]. This preferential sublattice adsorption is also found in the hydrogenation of metal supported graphene, where the underlying metal lattice often plays an important role.

Ng et al. have shown that on the weakly interacting metal-graphene systems such as graphene/Ir(111) and graphene/Pt(111) H atoms form a graphone-like structure in the valleys of the moiré

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pattern [13] which is caused by a lattice mismatch between the graphene and the metal lattice. On the strongly bound and lattice matched graphene/Ni(111) system, however, a blocking of not only one sublattice, but also of nearest neighbour adsorption sites of the same sublattice has been observed [13]. This is in good agreement with our findings, as will be discussed later. On the other hand, on the same graphene/Ni(111) system, a full hydrogenation of one sublattice, and therefore the synthesis of graphone was found in a different study [8]. The major difference between the two studies is that in the latter one, hydrogenation took place at a much lower temperature (170 K compared to 300 K).

On graphene/SiC, dimer formation at low coverage and disordered cluster formation at high coverage have been observed. In contrast to the graphite(0001) surface, hydrogen monomers were also found on graphene/SiC, suggesting a stronger binding to the surface in this case [14,15]. On graphene/Cu(111), a structural arrangement has been observed by scanning tunnelling microscopy (STM) [1], where three different configurations were found, all with a preference to sublattice adsorption. Such a sublattice configuration is predicted to cause ferromagnetism in graphene [16]. These effects are linked to the fact that the adsorption of an H atom on a graphene surface creates a distortion in both electron and spin density that exhibits a $(\sqrt{3} \times \sqrt{3})\mathbf{R}30°$ overstructure and that extends over several nm, as shown by ab-initio calculations and STM/atomic-force microscopy (AFM) measurements [17–19].

Directly connected to the question of an ordered hydrogenation is the question if a diffusion of H adatoms on the graphene/Ni(111) surface is in general possible (i.e., if the diffusion barrier is lower than the desorption barrier) and, if possible, at what rates it would occur. On the graphene/Ni(111) surface, density-functional theory (DFT) calculations predict a diffusion barrier of 1.9 eV, which is lower than the desorption barrier for a single H atom of 2.25 eV [8]. Quantum transition-state theory (TST) calculations predict H atom diffusion on a free-standing graphene surface with a diffusion barrier of 0.71 eV [20]. DFT calculations predict a diffusion barrier of 1.25 eV for single H atoms, but only 0.46 eV for an H atom in the vicinity of a second atom [21]. On a graphene bilayer, Kinetic Monte Carlo (KMC) calculations predict dimer formation via diffusion and subsequent desorption within a few minutes [22].

Here, we present our findings from helium atom scattering (HAS). Various pristine graphene/metal systems have been studied successfully with HAS previously, where precise values for the surface Debye temperature, electronic corrugation, or possible moiré patterns could be determined [23–29]. Notably, neutral He atom beams with energies in the order of 5–10 meV are perfectly suited to probe H overlayers in an inert, completely non-destructive manner. HAS provides, furthermore, a precise probe for both adsorbate coverage and adsorbate structure due to the very large scattering cross section of surface defects and adsorbed molecules [30]. This allowed us to study both, hydrogen sorption kinetics and structural adsorbate ordering. In addition, the spin-echo technique allowed us to gain information on surface dynamics in a time range from sub-picoseconds to about 1 ns. We made use of this to exclude a diffusion of H atoms over a large time scale.

2. Experimental details

2.1. Hydrogenation of graphene/Ni(111)

All measurements have been performed on the Cambridge helium-3 spin-echo spectrometer (HeSE) [31,32]. We have published the characterisation and growth of the graphene layer on a Ni(111) surface elsewhere [33]. Briefly, the nickel (Ni) (111) single crystal used in the study was a disc with a diameter of 10 mm and a thickness of 1 mm. The crystal was mounted on a sample holder,

which can be heated using radiative heating from a filament on the backside of the crystal or cooled down to 100 K using liquid nitrogen or 45 K using liquid helium, respectively. The sample temperature was measured using a chromel-alumel thermocouple. Prior to the measurements, the surface was cleaned by Ar^+ sputtering and annealing at 870 K. A monolayer of graphene on Ni(111) was grown by dosing ethene (C_2H_4) while heating the Ni crystal (730 K) over several hours.

In a series of experiments, the graphene/Ni(111) sample was heated to different temperatures and hydrogen gas was injected into the vacuum chamber using a microcapillary array beam doser at a distance of 50 mm to the sample. A cracking filament (4 A, 1 V DC) was used to produce atomic hydrogen. A mass spectrometer was routinely used during all measurements to exclude possible contaminations of the chamber.

We studied the hydrogen adsorption kinetics by monitoring the attenuation of the specular helium-scattering signal during hydrogenation of the graphene surface. Adsorption was monitored at 400–700 K at a dosing pressure at the surface of $3 \cdot 10^{-6}$ mbar. Subsequently, isothermal desorption was monitored at different temperatures using the same approach.

2.2. Diffraction and spin-echo measurements

After a maximum possible hydrogenation of the graphene surface (confirmed by a maximum attenuation of the specular scattering signal), helium diffraction studies were performed in the fixed $44.4°$ source − detector scattering geometry of the HeSE apparatus. The surface temperature of 400 K was chosen because a contamination through intercalation at defect sites cannot be ruled out at room temperature, although the graphene/Ni(111) surface is highly inert. In the case of HAS, the momentum transfer $\Delta\mathbf{k}$ can be separated into a component parallel to the surface and perpendicular to the surface (designated by subscript z): $\Delta\mathbf{k} = (\Delta\mathbf{K}, \Delta k_z)$. For a diffraction scan the momentum transfer parallel to the surface, given by $|\Delta\mathbf{K}| = |\mathbf{k_i}|(\sin(\gamma_f) - \sin(\gamma_i))$, is varied by changing the incident angle γ_i. Here, $\mathbf{k_i}$ is the incident wave vector and γ_i and γ_f are the incident and final angle with respect to the surface normal, respectively.

Helium spin-echo measurements were subsequently performed in the same set-up at temperatures of 400, 500 and 600 K, respectively. At 500 and 600 K, a constant H overpressure was applied to ensure a constant surface coverage despite desorption. In spin-echo spectroscopy the intermediate scattering function (ISF), $I(\Delta K, t)$, is directly measured in form of a polarisation amplitude [34]. Structural reconfigurations of the surface from e.g. adsorbate diffusion cause a decay of $I(\Delta K, t)$ over the spin-echo time, t. For simple diffusional processes this decay bears the shape of an exponential decay [35].

3. Results and discussion

3.1. Isothermal hydrogen adsorption

Adsorption measurements were performed by monitoring the specularly reflected helium signal in real time while exposing the graphene surface to a constant partial pressure of atomic hydrogen, that had been dissociated by a cracking filament. This was repeated at different surface temperatures in the range 400–700 K. Adsorption was observed up to temperatures below 600 K, above which an adsorption-desorption equilibrium was rapidly reached and thus no substantial scattering-signal attenuation occurred.

Fig. 1 shows the specularly reflected helium-scattering signal during adsorption of atomic hydrogen on the graphene/Ni(111) surface for three different temperatures: 400 K, 500 K, and 550 K. In